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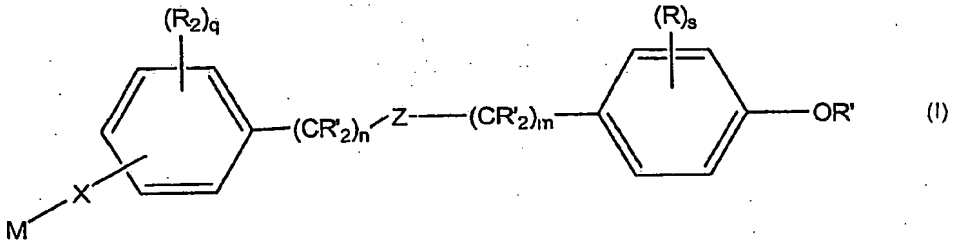

(I)

(57) Abstract: Alkylated antioxidant macromolecules are represented by Structural Formula (I), wherein the variables are described herein. Also included are methods of making the molecules and methods of using the molecules as antioxidants.

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ALKYLATED AND POLYMERIC MACROMOLECULAR ANTIOXIDANTS AND METHODS OF MAKING AND USING THE SAME

RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/665,638, filed on March 25, 2005. The entire teachings of the above application are incorporated herein by reference.

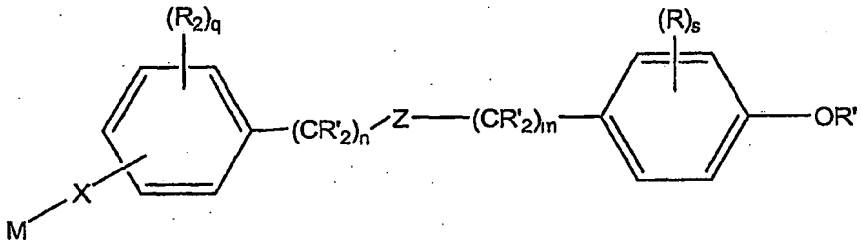
BACKGROUND OF THE INVENTION

Antioxidants are employed to prevent oxidation in a wide range of materials, for example, plastics, elastomers, lubricants, petroleum based products (lubricants, gasoline, aviation fuels, and engine oils), cooking oil, cosmetics, processed food products, and the like. While many antioxidants exist, there is a continuing need for new antioxidants that have improved properties.

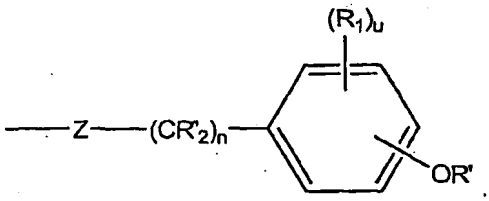
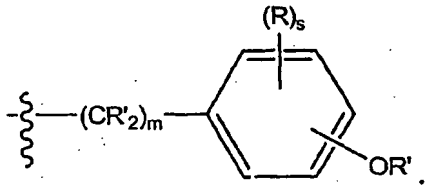
SUMMARY OF THE INVENTION

The present invention relates to alkylated and polymeric antioxidant macromolecules that in general have improved antioxidant properties.

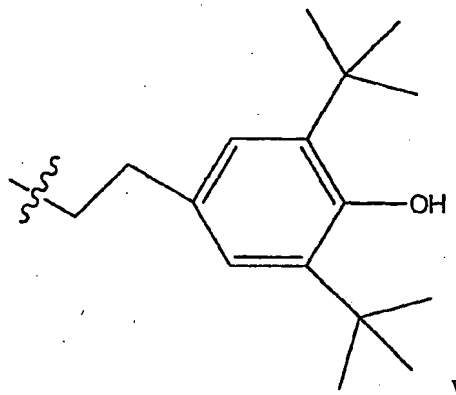
In one embodiment the present invention is directed to compounds represented Structural Formula 1:



1

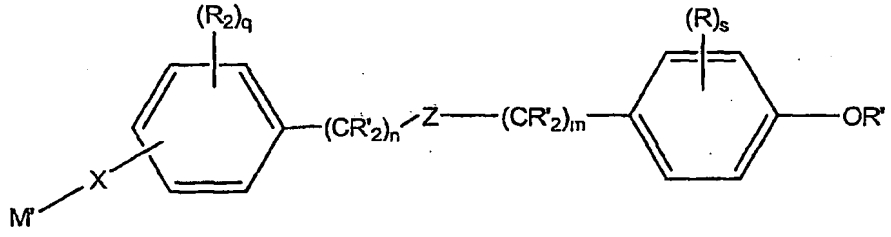
Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -O-, -S-, -C(O)OC(O)- or a bond. Each R' is independently -H or optionally substituted alkyl. Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH, or  . Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -O-, -S-, -NR'- or -C(O)OC(O)-. M is an alkyl or  . Each n and m are independently integers from Oto 6. Each s, q and u are

independently integers from Oto 4. In certain embodiments M is not



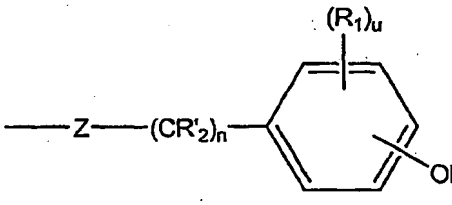
when X is -C(O)O- or -OC(O)-.

In another embodiment, the present invention is directed to polymers represented by Structural Formula 2:

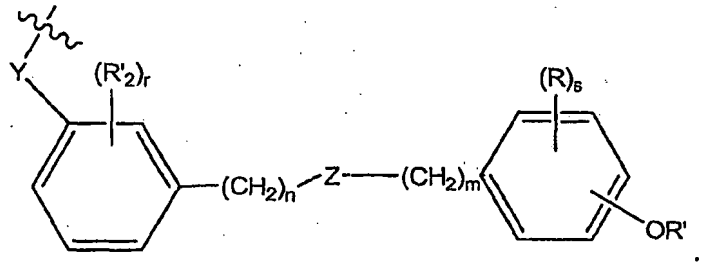


2

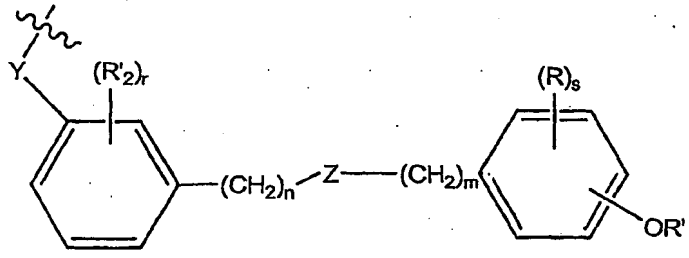
Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond. Each R' is independently -H or optionally substituted alkyl. Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,



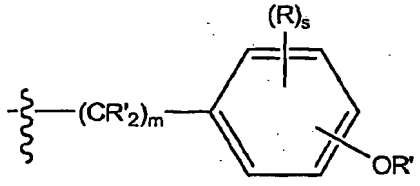
-OH, $-NH_2$, -SH, or . Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH



or . Each R'_2 is independently -M'-X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH

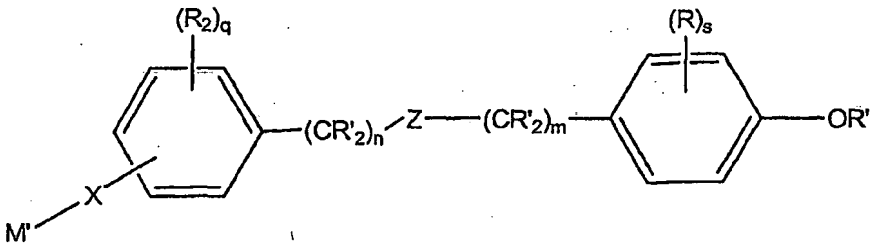


or . X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -O-, -S-, -NR'- or -C(O)OC(O)-. Each Y is independently Q-W-Q'. Each Q is independently an optionally substituted C1-C20 alkylene group. Each Q' is independently a bond or an optionally substituted C1-C20 alkylene group. Each W is independently arylene, -0-, -S-, -NR'-, -N(OR')-, -C(=N(0R'))-, -C(O)NR'-, -NR'C(O)-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -C(O)OC(O)-, or a bond. Each M' is independently -H,



alkyl, or . Each n and m are independently integers from Oto 6. Each s, q and u are independently integers from Oto 4. r is an integer from Oto 4.

In another embodiment, the present invention is directed to compositions comprising a compound represented by Structural Formula 1 (as defined herein) and a compound represented by Structural Formula 3:



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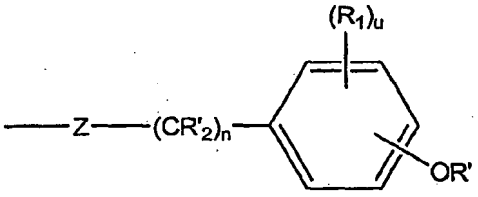
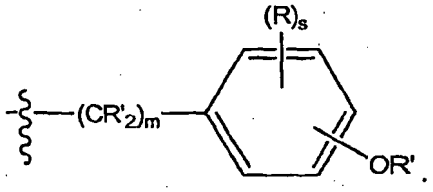
Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -O-, -S-, -C(O)OC(O)- or a bond. Each R' is independently -H or optionally substituted alkyl. Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,



-OH, $-NH_2$, -SH, or . Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -O-, -S-, -NR'- or -C(O)OC(O)-. M' is a -H, alkyl or



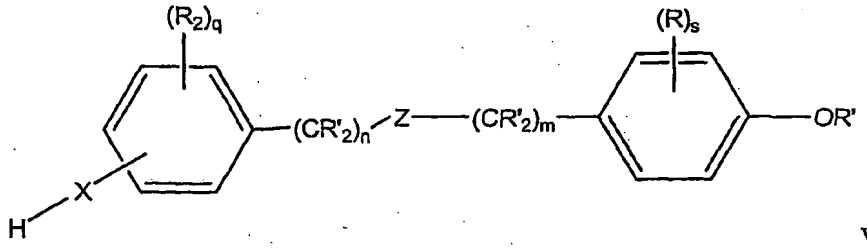
. Each n and m are independently integers from Oto 6. Each s, q and u are independently integers from Oto 4.

In another embodiment the present invention is directed to methods of inhibiting oxidation in an oxidizable material comprising combining the oxidizable material with a compound represented Structural Formula 1.

In another embodiment the present invention is directed to methods of inhibiting oxidation in an oxidizable material comprising combining the oxidizable material with a polymer represented Structural Formula 2.

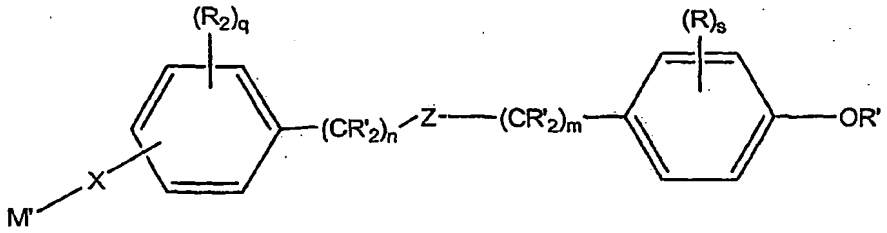
In another embodiment the present invention is directed to methods of inhibiting oxidation in an oxidizable material comprising combining the oxidizable material with a composition comprising a compound represented Structural Formula 1 and a compound represented Structural Formula 3.

In another embodiment the present invention is a method of making a compound represented by Structural Formula 1, comprising the steps of alkylating a compound represented by the following structural formula:



where the variables are described herein, with a haloalkyl and isolating the alkylated compound.

In another embodiment the present invention is a method of making a polymer represented by the following Structural Formula 3, comprising the steps of polymerizing a compound represented by the following structural formula:



where the variables are described herein, in the presence of an aldehyde and isolating the polymer.

In certain embodiments, the alkylated antioxidant macromolecules of the present invention can have enhanced antioxidant activity and better thermal stability compared to commercially available antioxidants.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

FIG 1 is a graph showing superior performance of an alkylated macromolecule of Formula III of the present invention with M = $C_{10}H_{21}$, compared with commercially available antioxidants.

FIG 2 is a high resolution nuclear magnetic resonance (NMR) spectrum of a compound of Formula III of the present invention having M=$C_{10}H_{21}$.

FIG 3 is a Fourier Transform Infrared (FT-IR) spectrum of a compound of Formula III of the invention having M=$C_{10}H_{21}$. The assignments of the peaks in FIG 3 are consistent with the structure of the compound.

FIG 4 and FIG 5 are graphs showing the melt flow index (MFI) results for antioxidants of the present invention versus Irganox® 1010.

FIG 6 and FIG 7 are graphs showing the color development results for antioxidants of the present invention versus Irganox® 1010.

FIG 8 is a graph showing the oxidative induction time (OIT) results for antioxidants of the present invention versus Irganox® 1010.

FIG 9 is a graph showing the heat aging results for antioxidants of the present invention versus Irganox® 1010, Irganox® 1330 and Irganox® 1076.

DETAILED DESCRIPTION OF THE INVENTION

A description of preferred embodiments of the invention follows.

In certain embodiments the compounds and polymers of the present invention comprise sterically hindered groups such as phenol groups. Sterically

hindered, as used herein means that the substituent group (e.g., bulky alkyl group) on a ring carbon atom adjacent (or alternatively *para)* to a ring carbon atom substituted with a phenolic hydroxy group (or thiol or amine group), is large enough to sterically hinder the phenolic hydroxy group (or thiol or amine groups). This steric hindrance, in certain embodiments results in more labile or weak bonding between the oxygen and the hydrogen (or ^ulfur or nitrogen and hydrogen) and in turn enhances the stability and antioxidant activity (proton donating activity) of the sterically hindered antioxidant.

Repeat units of the antioxidants of the invention include substituted benzene molecules. Some of these benzene molecules are typically based on phenol or a phenol derivative, such that they have at least one hydroxyl or ether functional group. hi certain embodiments, the benzene molecules have a hydroxyl group. The hydroxyl group can be a free hydroxyl group and can be protected or have a cleavable group attached to it (e.g., an ester group). Such cleavable groups can be released under certain conditions (e.g., changes in pH), with a desired shelf life or with a time-controlled release (e.g., measured by the half-life), which allows one to control where and/or when an antioxidant can exert its antioxidant effect. The repeat units can also include analogous thiophenol and aniline derivatives, e.g., where the phenol -OH can be replaced by -SH, -NH-, and the like.

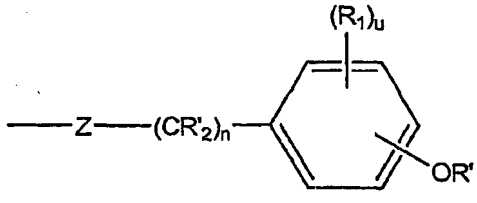
Substituted benzene repeat units of an antioxidant of the invention are also typically substituted with a bulky alkyl group or an n-alkoxycarbonyl group. In certain embodiments, the benzene monomers are substituted with a bulky alkyl group. In certain other embodiments, the bulky alkyl group is located *ortho* or *meta* to a hydroxyl group on the benzene ring, typically *ortho.* A "bulky alkyl group" is defined herein as an alkyl group that is branched *alpha-* or *beta-* to the benzene ring. hi certain other embodiments, the alkyl group is branched alpha to the benzene ring. In certain other embodiments, the alkyl group is branched twice alpha to the benzene ring, such as in a *tert*-butyl group. Other examples of bulky alkyl groups include isopropyl, 2-butyl, 3-pentyl, 1,1-dimethylpropyl, 1-ethyl-1-methylpropyl and 1,1-diethylpropyl. hi certain other embodiments, the bulky alkyl groups are unsubstituted, but they can be substituted with a functional group that does not interfere with the antioxidant activity of the molecule. Straight chained

alkoxylcarbonyl groups include methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, n-butoxycarbonyl and n-pentoxycarbonyl. N-propoxycarbonyl is a preferred group. Similar to the bulky alkyl groups, n-alkoxycarbonyl groups are optionally substituted with a functional group that does not interfere with the antioxidant activity of the molecule.

In certain embodiments for compounds represented by Structural Formula 1:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond. In certain other embodiments Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-. In certain other embodiments, Z is -C(O)NH- or -NHC(O)-. Optionally, Z is not -C(O)O-, -OC(O)-, -O- or -NH-. In various embodiments, the present invention relates to a compound of Structural Formula 1 and the attendant definitions, wherein Z is -OC(O)-. In another embodiment, Z is -C(O)O-. In another embodiment, Z is -C(O)NH-. In another embodiment, Z is -NHC(O)-. In another embodiment, Z is -NH-. In another embodiment, Z is -CH=N-. In another embodiment, Z is -C(O)-. In another embodiment, Z is -O-. In another embodiment, Z is -C(O)OC(O)-. In another embodiment, Z is a bond.

Each R' is independently -H or optionally substituted alkyl. In certain other embodiments R' is - H or an alkyl group. In certain other embodiments R' is - H or a Cl-ClO alkyl group. In certain other embodiments R' is -H.

Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH, or 

. In certain other embodiments, each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R is independently an alkyl or alkoxycarbonyl. In certain other embodiments each R is independently a C1-C6 alkyl or a C1-C6 alkoxycarbonyl. In certain other embodiments each R is independently *tert-butyl* or propoxycarbonyl. In certain other embodiments each R

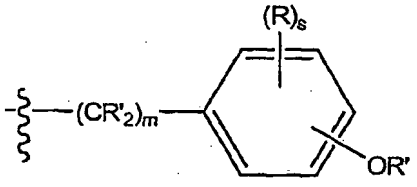
is independently an alkyl group. In certain embodiments each R is independently a bulky alkyl group. Suitable examples of bulky alkyl groups include butyl, sec-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like. In certain embodiments each R is *tert*-butyl. In certain embodiments at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R groups are *tert*-butyl. hi another embodiment, both R groups are *tert*-butyl adjacent to the OH group.

Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain other embodiments, each R_1 is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R_1 is independently an alkyl or alkoxycarbonyl. In certain other embodiments each R_1 is independently a C1-C6 alkyl or a C1-C6 alkoxycarbonyl. In certain other embodiments each R_1 is independently *tert*-butyl or propoxycarbonyl. In certain other embodiments each R_1 is independently an alkyl group, hi certain embodiments each R_1 is independently a bulky alkyl group. Suitable examples of bulky alkyl groups include butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like. In certain embodiments each R_1 is *tert*-butyl. In certain embodiments at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R_1 groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R_1 groups are *tert*-butyl. In another embodiment, both R_1 groups are *tert*-butyl adjacent to the OH group.

Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain other embodiments, each R_2 is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R_2 is independently an alkyl or alkoxycarbonyl. In certain other embodiments, each R_2 is independently an optionally substituted alkyl. In

certain other embodiment each R_2 is independently an alkyl. In certain other embodiments each R_2 is independently a Cl-ClO alkyl. In certain other embodiments each R_2 is independently a C1-C6 alkyl. In certain other embodiments each R_2 is independently a bulky alkyl group or a straight chained alkyl group. In certain other embodiments each R_2 is independently methyl, ethyl, propyl, butyl, sec-butyl, *tert*-butyl, 2-propyl or 1,1-dimethylhexyl. hi certain embodiments each R_2 is methyl or *tert*-butyl.

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-. In certain embodiments X is -NH-, -S- or -O-. In certain embodiments X is -0-. Optionally X is a bond.

M is an alkyl or 

. hi certain embodiment M is alkyl. In certain other embodiments M is a C1-C20 linear or branched chain alkyl. In certain other embodiments M is a C5-C20 linear or branched chain alkyl. Ih certain other embodiments M is decane.

Each n and m are independently integers from Oto 6. hi certain embodiments each n and m are independently integers from Oto 2.

In another embodiment, the present invention relates to a compound of Structural Formula 1 wherein n is o.

hi another embodiment, the present invention relates to a compound of Structural Formula 1 wherein m is 1.

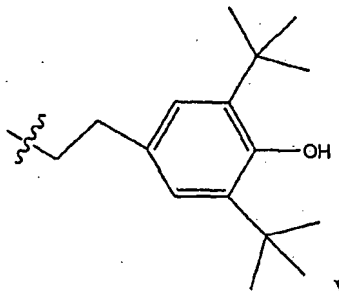
hi another embodiment, the present invention relates to a compound of Structural Formula 1 and the attendant definitions, wherein n is Oand m is 1.

In another embodiment, the present invention relates to a compound of Structural Formula 1 wherein n is o, m is 1, and Z is -C(O)O-.

In another embodiment, the present invention relates to a compound of Structural Formula 1 wherein n is o, m is 1, Z is -C(O)O-, and the two R groups adjacent to the OH are *tert*-butyl.

Each s, q and u are independently integers from Oto 4. In certain embodiments, each s and q are independently integers from Oto 2. In certain embodiments, s is 2.

In certain embodiments for compounds represented by Structural Formula 1



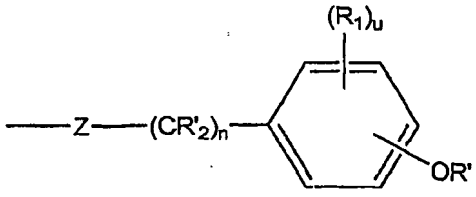
M is not when X is -C(O)O- or -OC(O)-.

In certain embodiments for polymers represented by Structural Formula 2:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond. In certain other embodiments Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-. In certain other embodiments, Z is -C(O)NH- or -NHC(O)-. Optionally, Z is not -C(O)O-, -OC(O)-, -O- or -NH-. In various embodiments, the present invention relates to a compound of Structural Formula 1 and the attendant definitions, wherein Z is -OC(O)-. In another embodiment, Z is -C(O)O-. In another embodiment, Z is -C(O)NH-. In another embodiment, Z is -NHC(O)-. In another embodiment, Z is -NH-. In another embodiment, Z is -CH=N-. In another embodiment, Z is -C(O)-. In another embodiment, Z is -0-. In another embodiment, Z is -C(O)OC(O)-. In another embodiment, Z is a bond.

Each R' is independently -H or optionally substituted alkyl. In certain other embodiments R' is - H or an alkyl group. In certain other embodiments R' is - H or a Cl-ClO alkyl group. In certain other embodiments R' is -H.

Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,

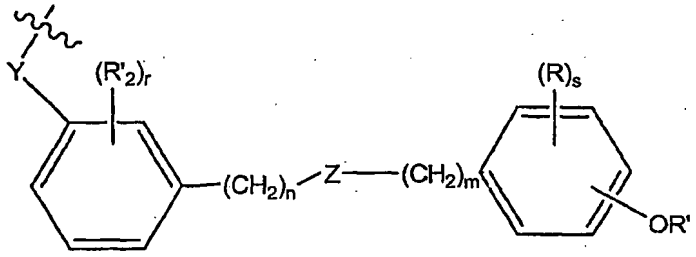


-OH, $-NH_2$, -SH, or . In certain other

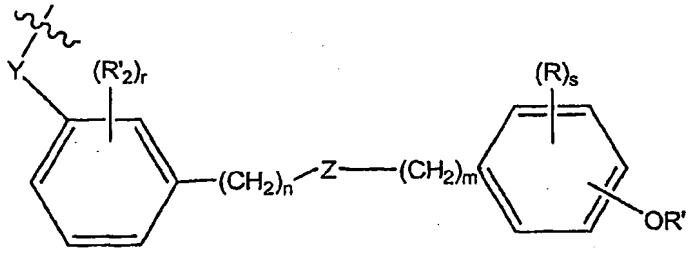
embodiments, each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R is independently an alkyl or alkoxycarbonyl. In certain other embodiments each R is independently a C1-C6 alkyl or a C1-C6 alkoxycarbonyl. In certain other embodiments each R is independently *tert*-butyl or propoxycarbonyl. In certain other embodiments each R is independently an alkyl group. In certain embodiments each R is independently a bulky alkyl group. Suitable examples of bulky alkyl groups include butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like. In certain embodiments each R is *tert*-butyl. In certain embodiments at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). hi certain other embodiments both R groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). Iri another embodiment, both R groups are *tert*-butyl. In another embodiment, both R groups are *tert*-butyl adjacent to the OH group.

Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain other embodiments, each R_1 is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R_1 is independently an alkyl or alkoxycarbonyl. In certain other embodiments each R_1 is independently a C1-C6 alkyl or a C1-C6 alkoxycarbonyl. In certain other embodiments each R_1 is independently *tert*-butyl or propoxycarbonyl. In certain other embodiments each R_1 is independently an alkyl group. In certain embodiments each R_1 is independently a bulky alkyl group. Suitable examples of bulky alkyl groups include butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like. In certain embodiments each R_1 is *tert*-butyl. hi certain embodiments at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both Ri groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R_1 groups are *tert*-butyl. hi another embodiment, both R_1 groups are *tert*-butyl adjacent to the OH group.

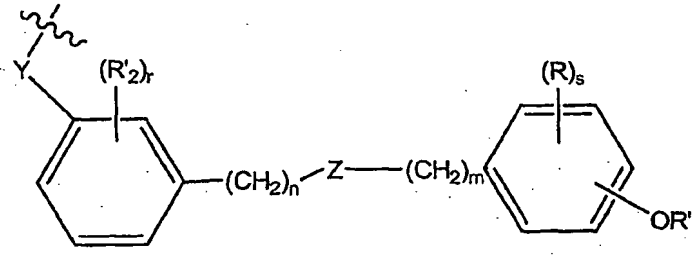
Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,



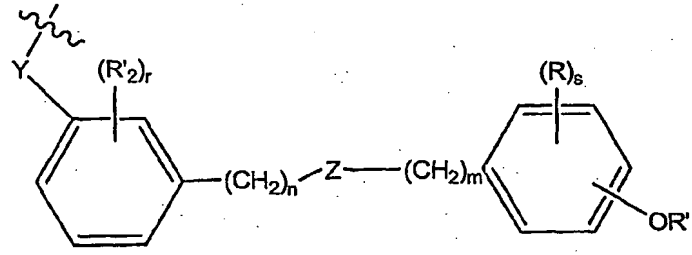
-OH, $-NH_2$, -SH or . In certain other embodiments, each R_2 is independently an optionally substituted alkyl, optionally substituted alkoxycarbonyl or



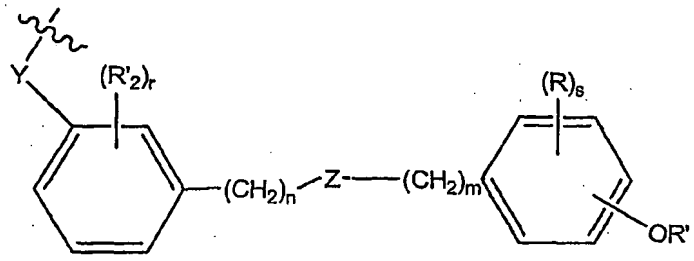
. In certain other embodiment each R_2 is independently an alkyl or alkoxycarbonyl or



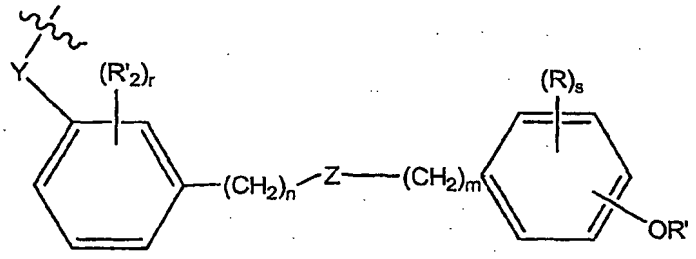
. In certain other embodiments, each R_2 is independently an optionally substituted alkyl or



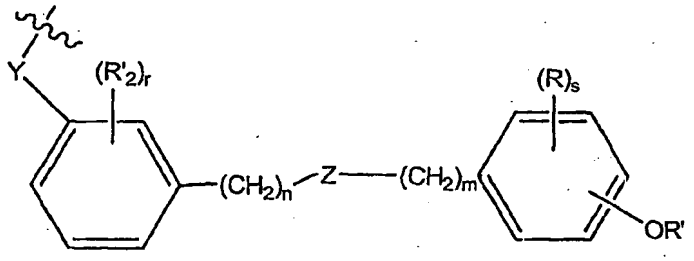
. In certain other embodiment each R_2 is independently an alkyl or



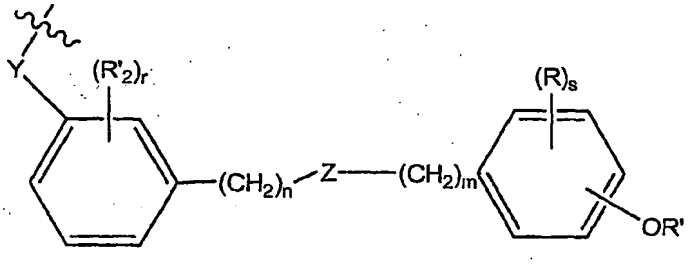
. In certain other embodiments each R_2 is independently a Cl-ClO alkyl or



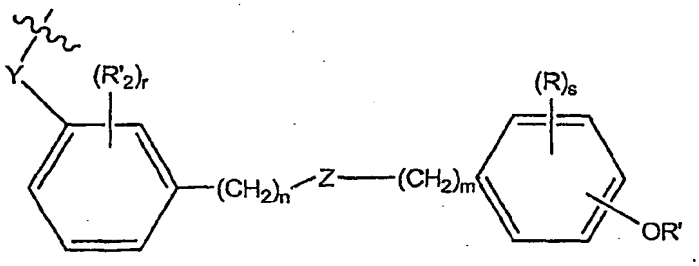
. In certain other embodiments each R_2 is independently a C1-C6 alkyl or



. In certain other embodiments each R_2 is independently a bulky alkyl group, a straight chained alkyl group or

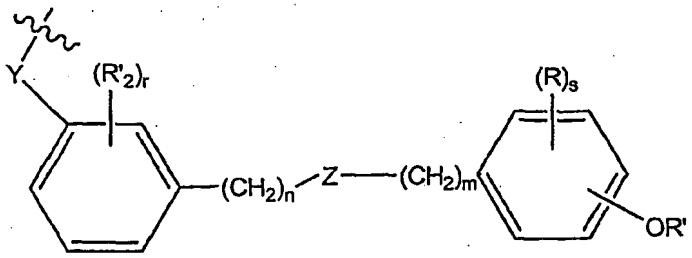


. In certain other embodiments each R_2 is independently methyl, ethyl, propyl, butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl or

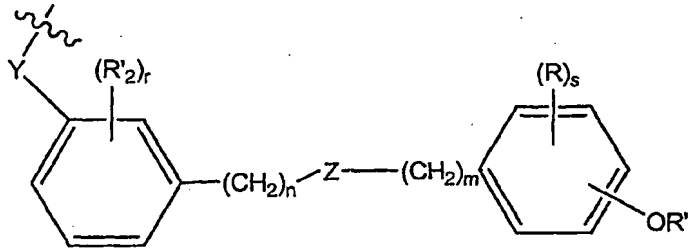


. In certain embodiments

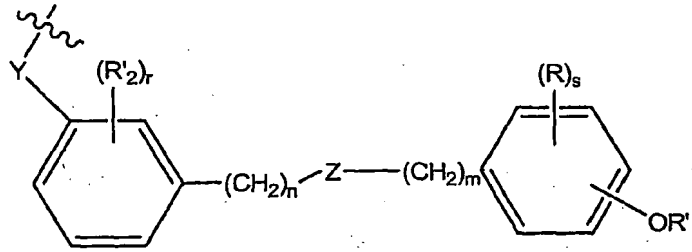
each R_2 is methyl, *tert-butyl* or



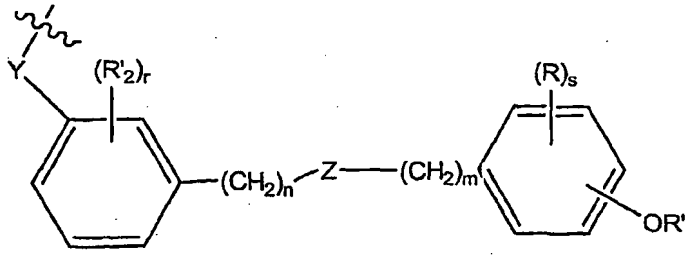
. Ih certain embodiments described in this paragraph one R_2 is:



. In certain embodiments described in this paragraph at least one R_2 is:



Each R'_2 is independently -M' -X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,

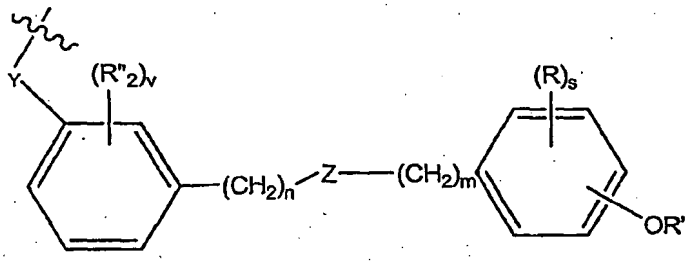


-OH, $-NH_2$, –SH or .

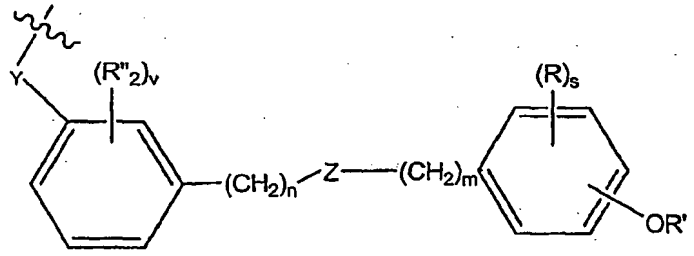
In one alternative embodiment for polymers represented by Structural Formula 2, each R'_2 is independently -M' -X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain embodiments, each R'_2 is independently -M'-X, an optionally substituted alkyl, or optionally substituted

alkoxycarbonyl. In certain embodiments, each R'_2 is independently -M'-X, an alkyl, or alkoxycarbonyl. In certain embodiments, each R'_2 is independently —M'-X or an alkyl. In certain embodiments, each R'_2 is independently -M'-X or a Cl-ClO alkyl. In certain embodiments, each R'_2 is independently -O-(Cl-C20-alkyl), -OH or C1-C6 alkyl. In certain other embodiments each R'_2 is independently -O-(C5-C20-alkyl), -OH, a linear alkyl group or a bulky alkyl group. Suitable examples of bulky alkyl groups include butyl, see-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like. In certain other embodiments each R'_2 is independently -O-(C5-C20-alkyl), -OH, methyl, ethyl, propyl, butyl, sec-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like.

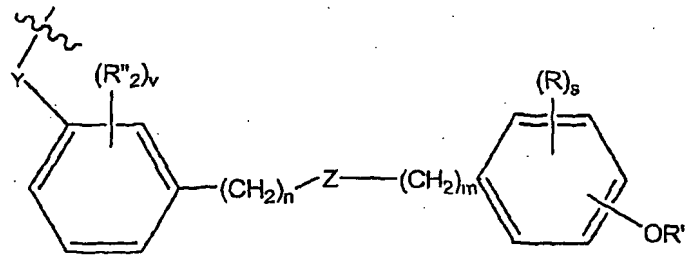
In another alternative embodiment for polymers represented by Structural Formula 2, each R'_2 is independently -M'-X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH or



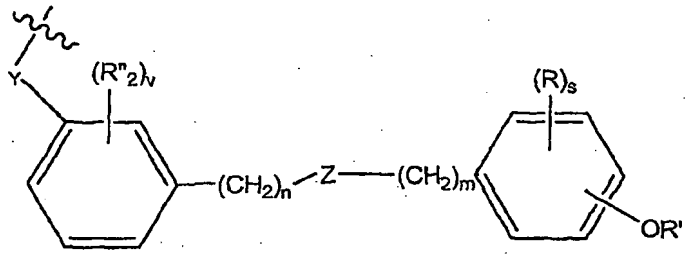
. In certain embodiments, each R'_2 is independently —M'-X, an optionally substituted alkyl,' optionally substituted alkoxycarbonyl or



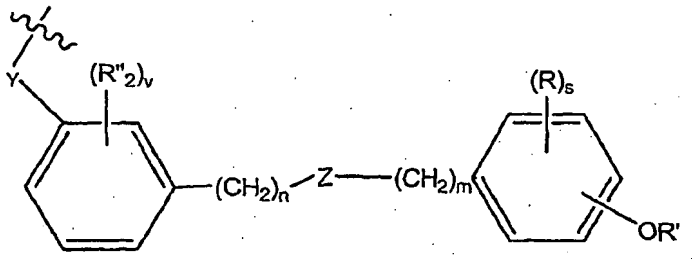
. In certain embodiments, each R'_2 is independently -M'-X, an alkyl, alkoxycarbonyl or



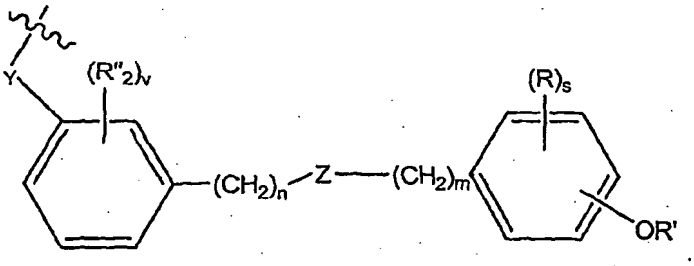
. In certain embodiments, eachR'2 is independently -M'-X, an alkyl or



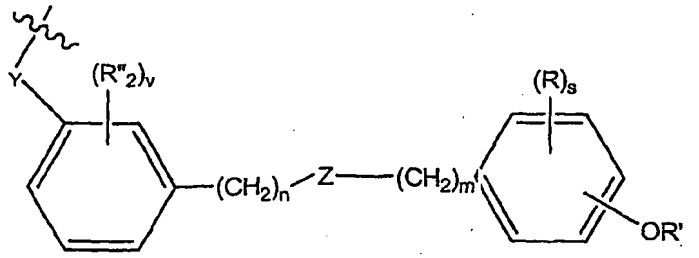
. In certain embodiments, each R'_2 is independently -M'-X or a Cl-ClO alkyl. In certain embodiments, each R'_2 is independently -O-(Cl-C20-alkyl), -O-H, C1-C6 alkyl or



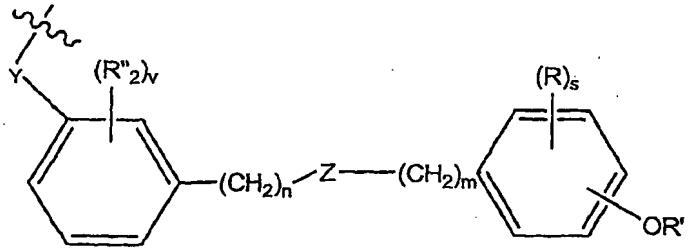
. In certain other embodiments each R'_2 is independently -O-(C5-C20-alkyl), -OH, a linear alkyl group or a bulky alkyl group, or



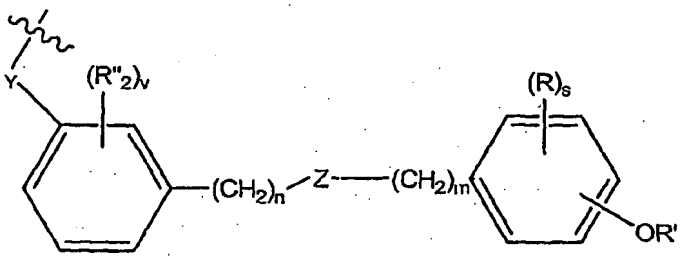
. Suitable examples of bulky alkyl groups include butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like. In certain other embodiments each R'_2 is independently -O-(C5-C20-alkyl), -OH, methyl, ethyl, propyl, butyl, sec-butyl, tert-butyl, 2-propyl, 1,1-dimethylhexyl, and the like or



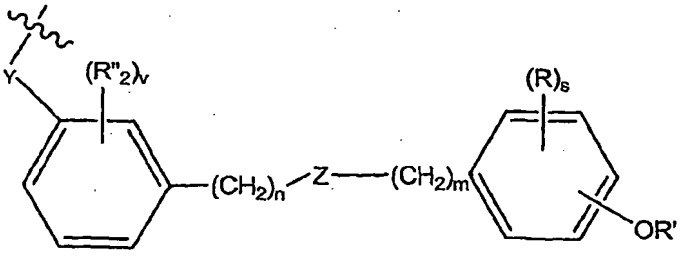
. In certain embodiments described in this paragraph at least one R'_2 is:



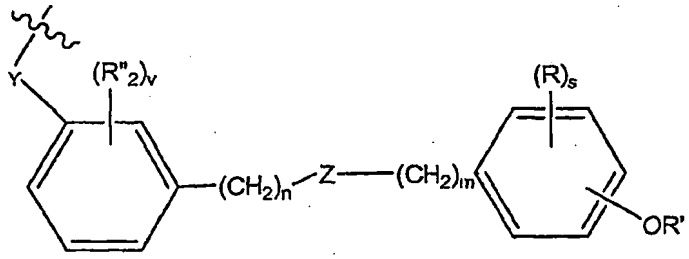
In certain embodiments, for polymers represented by Structural Formula 2, each $R"_2$ is independently -M'-X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH or



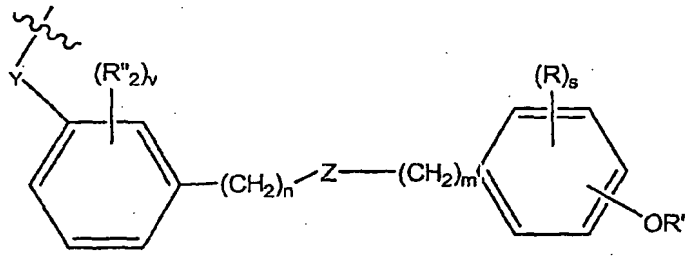
. In certain embodiments, each $R"_2$ is independently -M'-X, an optionally substituted alkyl, optionally substituted alkoxycarbonyl or



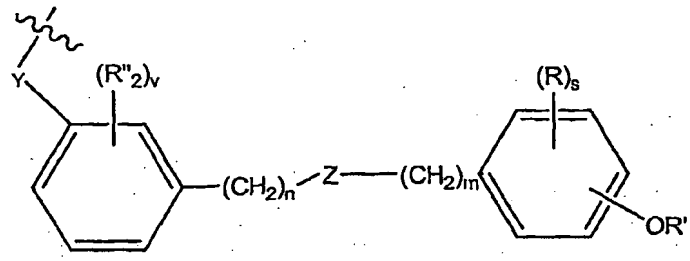
. In certain embodiments, each$R"_2$ is independently -M'-X, an alkyl, alkoxycarbonyl or



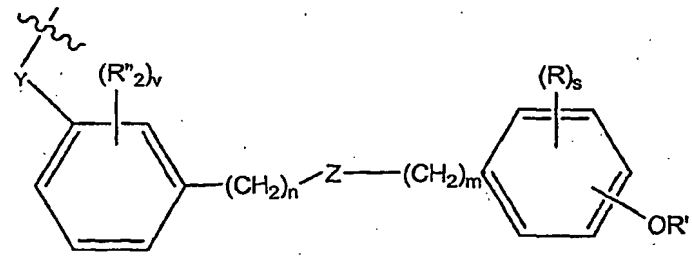
. In certain embodiments, each R"$_2$ is independently –M'-X, an alkyl or



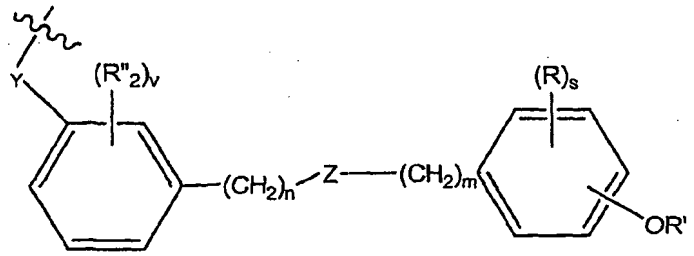
. In certain embodiments, each R"$_2$ is independently -M'-X or a Cl-ClO alkyl. In certain embodiments, each R"$_2$ is independently -O-(C 1-C20-alkyl), -O-H, C1-C6 alkyl or



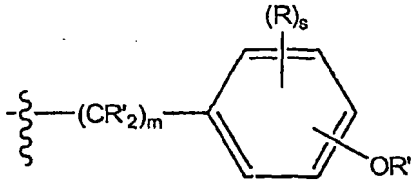
. h1 certain other embodiments each R"$_2$ is independently -O-(C5-C20-alkyl), -OH, a linear alkyl group or a bulky alkyl group, or



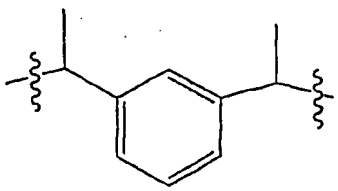
. Suitable examples of bulky alkyl groups include butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like. In certain other embodiments each R"$_2$ is independently -O-(C5-C20-alkyl), -OH, methyl, ethyl, propyl, butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like or



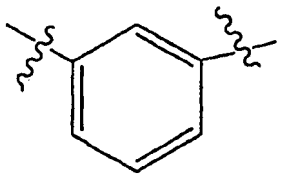
X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -O-, -S-, -NR'- or -C(O)OC(O)-. In certain embodiments X is -NH-, -S- or -O-. In certain embodiments X is -O-. Optionally X is a bond.

Each M' is independently -H, alkyl or  . In certain embodiments each M' is independently –H or alkyl. In certain other embodiments each M' is independently –H or a C1-C20 linear or branched chain alkyl. In certain other embodiments each M' is independently - H or a C5-C20 linear or branched chain alkyl. hi certain other embodiments each M' is independently - H or decane. In certain embodiments for polymers of the present invention represented by Structural Formula 2 at least one M' is not –H. In certain embodiments for polymers of the present invention represented by Structural Formula 2 at least one R'_2 is -M'-X.

Each Y is independently Q-W-Q'. In certain embodiments, Y is Q-W-Q' as defined below, which in certain embodiments is $-(CR'_2)_p$ -, $-(CR'_2)_p$-phenylene-(CR''_2)p-or-(CR''_2)pN(OH)$(CR''_2)_p$-. In certain embodiments, Y is Q-W-Q' as defined below, which in certain embodiments is -CR'V, $-CR''_2$-phenylene-CR''_2- or $-CR''_2N(OH)CR''_2$-. In certain embodiments Y is Q-W-Q' as defined below, which in certain embodiments is $-CH_2$, $-CH_2N(OH)CH_2$- or



. Additional values for Y are $-CH_2$, -N(OH)- or



Each Q is independently an optionally substituted C1-C20 alkylene group. In certain embodiments, each Q is independently an optionally substituted Cl-ClO alkylene group. In certain embodiments, each Q is independently -$(CH_2)_{1-10}$-, $CH(CH_3)$ or $C(CH_3)_2$. hi certain embodiments, each Q is independently -CH_2-, $CH(CH_3)$ or $C(CH_3)_2$.

Each Q' is independently a bond or an optionally substituted C1-C20 alkylene group. In certain embodiments, each Q' is independently a bond or an optionally substituted Cl-ClO alkylene group. In certain embodiments, each Q' is independently -$(CH_2)_{M\,0}$-, $CH(CH_3)$ or $C(CH_3)_2$. Li certain embodiments, each Q' is independently a bond, -CH_2-, $CH(CH_3)$ or $C(CH_3)_2$.

Each W is independently arylene, -O-, -S-, -NR'-, -N(OR')-, -C(=N(OR'))-, -C(O)NR'-, -NR'C(O)-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -C(O)OC(O)- or a bond. hi certain embodiments, each W is independently arylene, -O-, -S-, -NH-, -N(OH)-, -C(=N(OH))- or a bond. In certain embodiments W is a bond, phenylene or -N(OH)-.

Each R" is independently -H or optionally substituted alkyl. Ii certain embodiments, each R" is independently - H or alkyl. In certain embodiments, each R" is independently - H or a linear or branched Cl-ClO alkyl. hi certain embodiments, each R" is - H or a C1-C3 linear or branched alkyl. hi certain embodiments each R" is -H.

Each n and m are independently integers from Oto 6. hi certain embodiments, each n and m are independently integers from Oto 2.

hi another embodiment, the present invention relates to a polymer of Structural Formula 2 wherein n is o.

In another embodiment, the present invention relates to a polymer of Structural Formula 2 wherein m is 1.

In another embodiment, the present invention relates to a polymer of Structural Formula 2 wherein n is 0 and m is 1.

In another embodiment, the present invention relates to a polymer of Structural Formula 2 wherein n is 0, m is 1, and Z is -C(O)O-.

In another embodiment, the present invention relates to a polymer of Structural Formula 2 wherein n is 0, m is 1, Z is -C(O)O-, and the two R groups adjacent to the OH are *tert*-butyl.

Each s, q and u are independently integers from 0 to 4. In certain embodiments, q is an integer from 1 to 3. In certain embodiments, s is 2.

Each r is an integer from 0 to 4. In certain embodiments, each s and r are independently integers from 0 to 2. In certain embodiments each r and q are independently integers from 1 to 3.

Each v is an integer from 0 to 4. In certain embodiments each s and v are independently integers from 0 to 2.

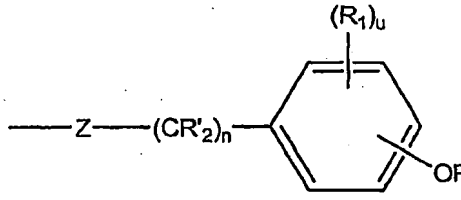
Each p is independently an integer of 1 to 5.

In certain embodiments for compounds represented by Structural Formula 3:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -O-, -S-, -C(O)OC(O)- or a bond. In certain other embodiments Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-. In certain other embodiments, Z is -C(O)NH- or -NHC(O)-. Optionally, Z is not -C(O)O-, -OC(O)-, -O- or -NH-. In various embodiments, the present invention relates to a polymer of Structural Formula 2 and the attendant definitions, wherein Z is -OC(O)-. In another embodiment, Z is -C(O)O-. In another embodiment, Z is -C(O)NH-. In another embodiment, Z is -NHC(O)-. In another embodiment, Z is -NH-. In another embodiment, Z is -CH=N-. In another embodiment, Z is -C(O)-. In another embodiment, Z is -O-. In another embodiment, Z is -C(O)OC(O)-. In another embodiment, Z is a bond.

Each R' is independently -H or optionally substituted alkyl. In certain other embodiments R' is - H or an alkyl group. In certain other embodiments R' is - H or a Cl-ClO alkyl group. In certain other embodiments R' is -H.

Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,



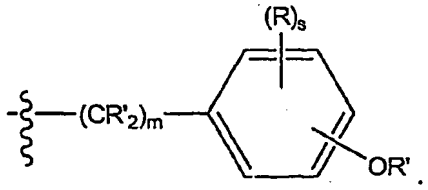
-OH, $-NH_2$, -SH, or . In certain other embodiments, each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R is independently an alkyl or alkoxycarbonyl. In certain other embodiments each R is independently a C1-C6 alkyl or a C1-C6 alkoxycarbonyl. In certain other embodiments each R is independently *tert*-butyl or propoxycarbonyl. In certain other embodiments each R is independently an alkyl group, hi certain embodiments each R is independently a bulky alkyl group. Suitable examples of bulky alkyl groups include butyl, .sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like. In certain embodiments each R is *tert*-butyl. In certain embodiments at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, see-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R groups are *tert*-butyl. In another embodiment, both R groups are *tert*-butyl adjacent to the OH group.

Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain other embodiments, each R_1 is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R_1 is independently an alkyl or alkoxycarbonyl. In certain other embodiments each R_1 is independently a C1-C6 alkyl or a C1-C6 alkoxycarbonyl. In certain other embodiments each R_1 is independently *tert*-butyl or propoxycarbonyl. In certain other embodiments each R_1 is independently an alkyl group. In certain embodiments each R_1 is independently a bulky alkyl group. Suitable examples of bulky alkyl groups include butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like. In certain embodiments each R_1 is *tert*-butyl. In certain embodiments at least one R_1 adjacent to the -OH group is a bulky

alkyl group (e.g., butyl, sec-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R_1 groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R_1 groups are *tert*-butyl. In another embodiment, both R_1 groups are *tert*-butyl adjacent to the OH group.

Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain other embodiments, each R_2 is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl. In certain other embodiment each R_2 is independently an alkyl or alkoxycarbonyl. In certain other embodiments, each R_2 is independently an optionally substituted alkyl. hi certain other embodiment each R_2 is independently an alkyl. hi certain other embodiments each R_2 is independently a Cl-ClO alkyl. In certain other embodiments each R_2 is independently a C1-C6 alkyl. In certain other embodiments each R_2 is independently a bulky alkyl group or a straight chained alkyl group. In certain other embodiments each R_2 is independently methyl, ethyl, propyl, butyl, sec-butyl, *tert*-butyl, 2-propyl or 1,1-dimethylhexyl. hi certain embodiments each R_2 is methyl or *tert*-butyl.

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-. In certain embodiments X is -NH-, -S- or -0-. In certain embodiments X is -0-. Optionally X is a bond.

Each M' is independently -H, alkyl or 

. In certain embodiments each M' is independently - H or alkyl. hi certain other embodiments each M' is independently - H or a C1-C20 linear or branched chain alkyl. hi certain other embodiments each M' is independently - H or a C5-C20 linear or branched chain alkyl. hi certain other embodiments each M' is independently - H or decane. hi certain other embodiments each M' is -H.

Each n and m are independently integers from Oto 6. In certain embodiments each n and m are independently integers from Oto 2.

In another embodiment, the present invention relates to a composition comprising a compound of Structural Formula 1 and a compound of Structural Formula 3 wherein n is 0.

LQ another embodiment, the present invention relates to a composition comprising a compound of Structural Formula 1 and a compound of Structural Formula 3 wherein m is 1.

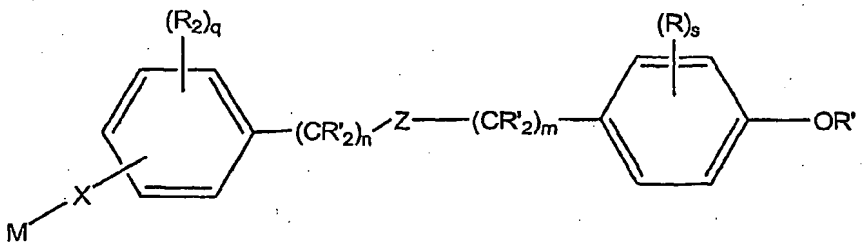
In another embodiment, the present invention relates to a composition comprising a compound of Structural Formula 1 and a compound of Structural Formula 3 wherein n is 0 and m is 1.

In another embodiment, the present invention relates to a composition comprising a compound of Structural Formula 1 and a compound of Structural Formula 3 wherein n is 0, m is 1, and Z is -C(O)O-.

In another embodiment, the present invention relates to a composition comprising a compound of Structural Formula 1 and a compound of Structural Formula 3 wherein n is 0, m is 1, Z is -C(O)O-, and the two R groups adjacent to the OH are *tert*-butyl.

Each s, q and u are independently integers from 0 to 4. In certain embodiments, each s and q are independently integers from 0 to 2. In certain embodiments, s is 2.

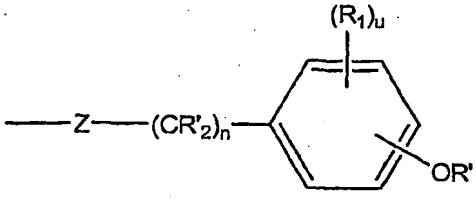
In a first embodiment the present invention is directed to a compound represented by Structural Formula 1:



1

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond.

Each R' is independently -H or optionally substituted alkyl.

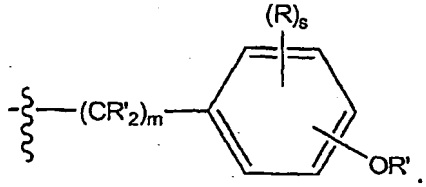
Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, 

-OH, $-NH_2$, -SH, or . In certain embodiments at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert-hutyl*, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R groups are *t*ert-butyl. In another embodiment, both R groups are *tert*-butyl adjacent to the OH group.

Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain embodiments at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R_1 groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R_1 groups are *tert*-butyl. In another embodiment, both R_1 groups are *tert*-butyl adjacent to the OH group.

Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH.

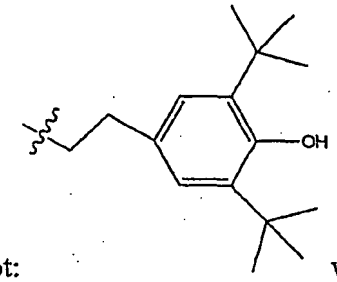
X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-. Optionally an additional value of X is a bond.

M is an alkyl or 

.

Each n and m are independently integers from Oto 6.

Each s, q and u are independently integers from 0 to 4. In certain embodiments for compounds of Structural Formula 1 M is



not: when X is -C(O)O- or –OC(O)-.

In a second embodiment of the present invention directed to a compound represented by Structural Formula 1:

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-.

R' is -H.

Each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl.

Each R_2 is independently an optionally substituted alkyl.

X is -O-.

M is an alkyl. In certain embodiments M is a C1-C20 alkyl.

Each n and m are independently integers from Oto 2.

each s and q are independently integers from Oto 2, and the remainder of the variables are as described above in the first embodiment.

In a third embodiment of the present invention directed to a compound represented by Structural Formula 1:

Z is -C(O)NH- or -NHC(O)-.

Each R is independently an alkyl or an alkoxycarbonyl.

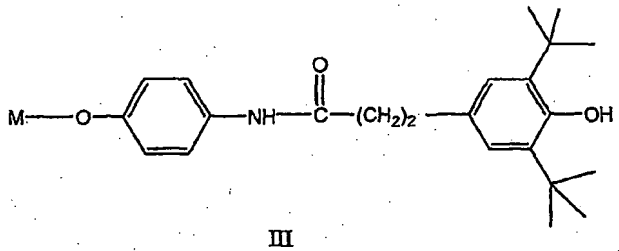
Each R_2 is independently an alkyl.

s is 2, and the remainder of the variables are as described above in the second embodiment.

In a fourth embodiment of the present invention directed to a compound represented by Structural Formula 1:

Each R is independently an alkyl group, and the remainder of the variables are as described above in the third embodiment. In certain embodiments each R is a bulky alkyl group. In certain embodiments two R groups are bulky alkyl groups adjacent to the - H group. hi certain embodiments the two R groups are *tert-buiyl* groups adjacent to the -OH group.

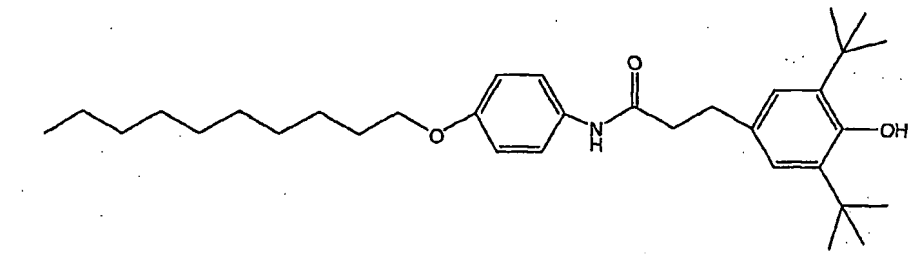
In a fifth embodiment of the present invention directed to a compound represented by Structural Formula 1, the compound is represented by Structural Formula III:

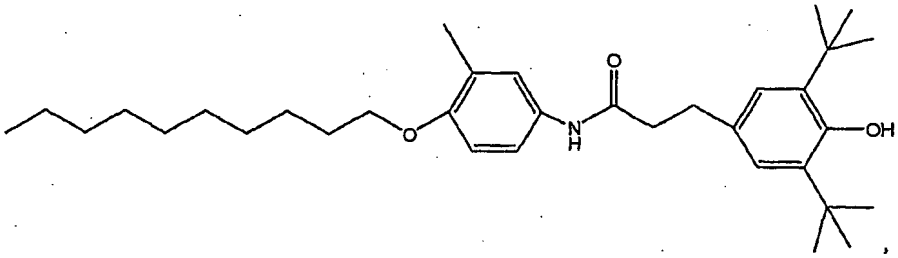


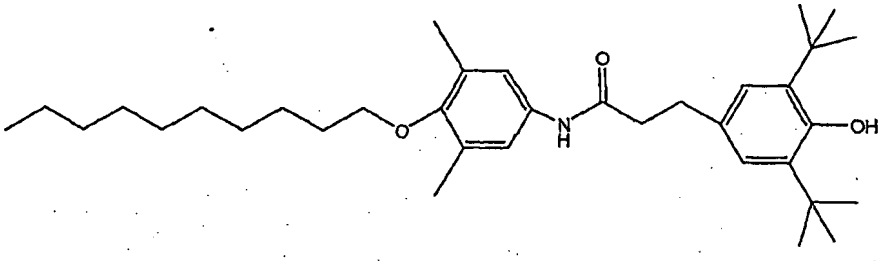
III

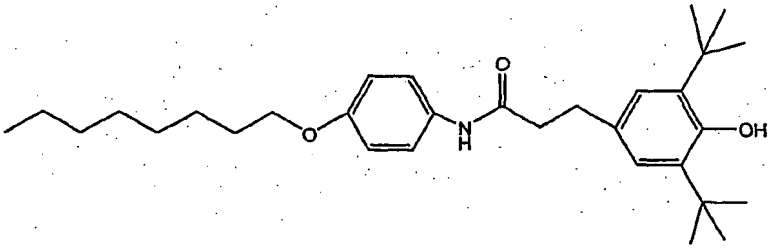
M is a Cl to C20 linear or branched alkyl chain.

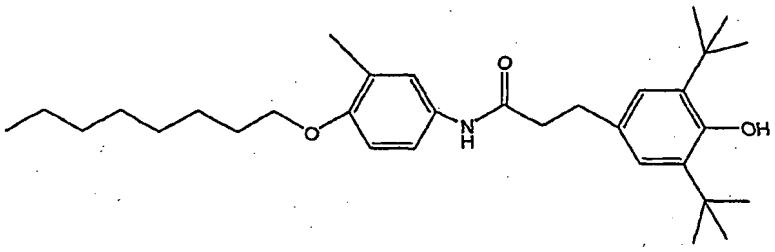
In a sixth embodiment of the present invention directed to a compound represented by Structural Formula 1, the compound is represented by a Structural Formula selected from:

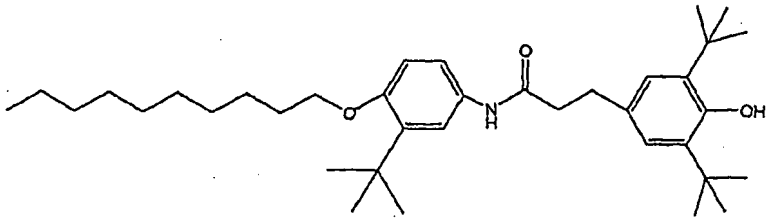


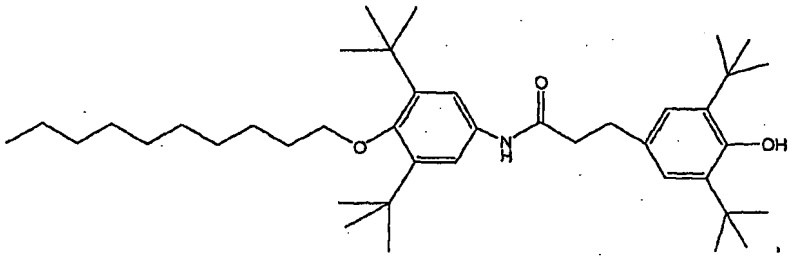


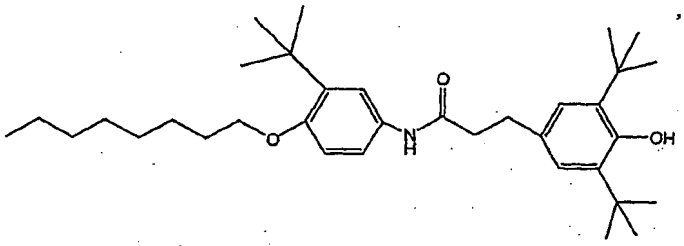


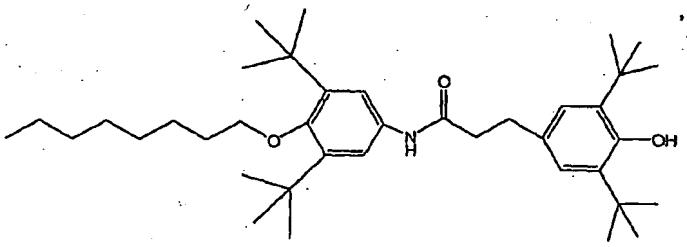


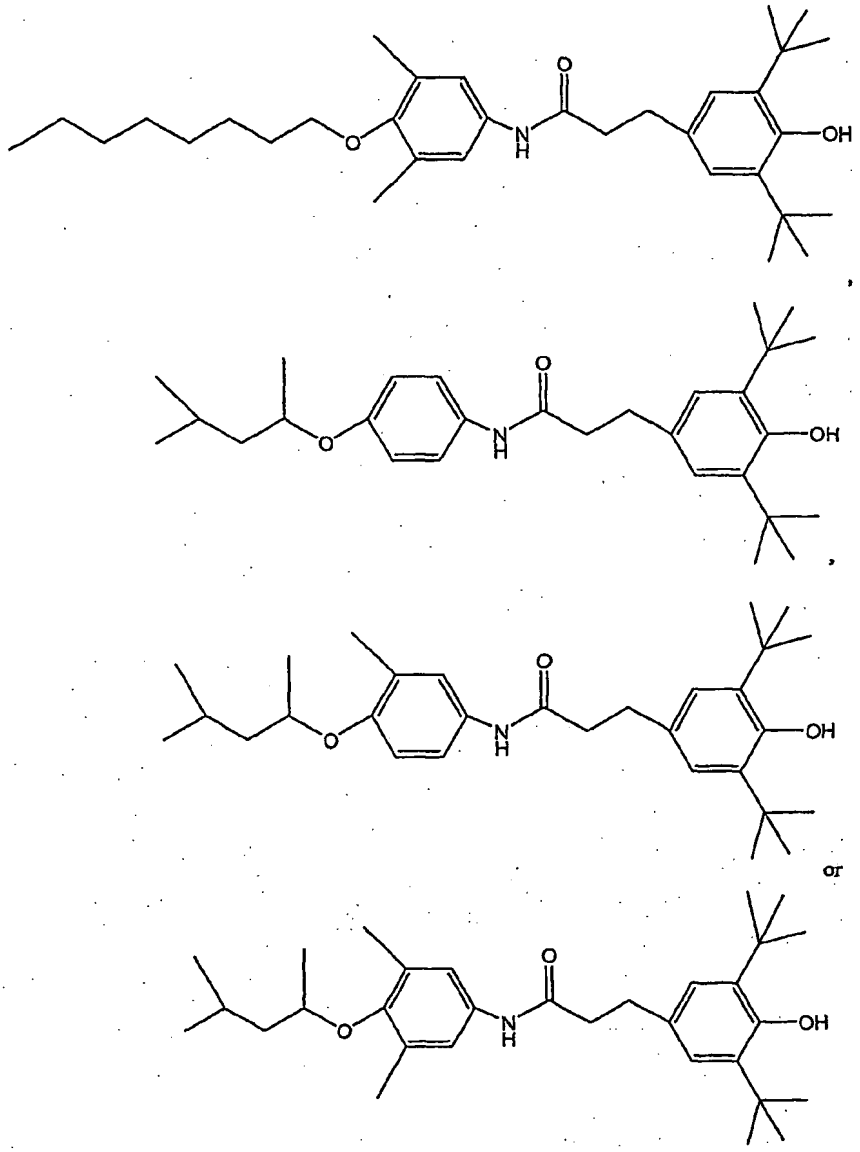



O
N
H
O
OH


O
N
H
O
OH

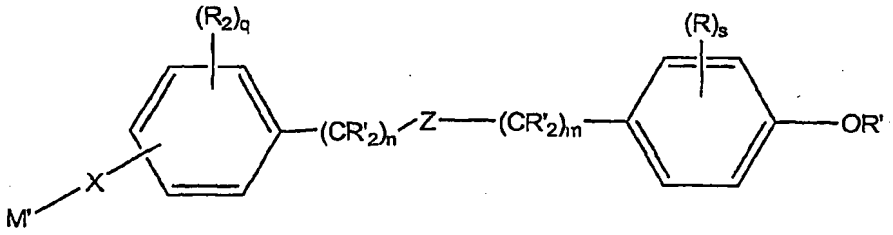

O
N
H
O
OH


O
N
H
O
OH



In certain embodiment the present invention is directed to polymers comprising at least two repeat units at least one of which is represented by Structural Formula 1. In certain other embodiments the present invention is directed to polymers comprising at least two repeat units at least one of which is Structural Formula 1 where an additional value for M can be -H and the repeat units are connected by at least one methylene group.

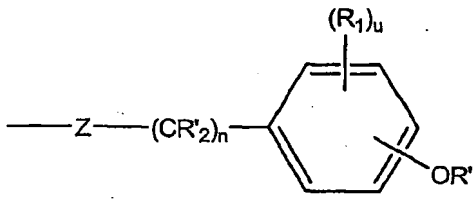
In a first embodiment of the present invention directed to a polymer represented by Structural Formula 2:



Z is -C(O)NR'-, -NR5C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -O-, -S-, -C(O)OC(O)- or a bond.

Each R' is independently -H or optionally substituted alkyl.

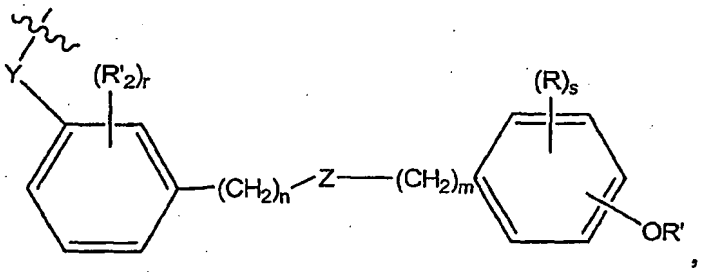
Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,

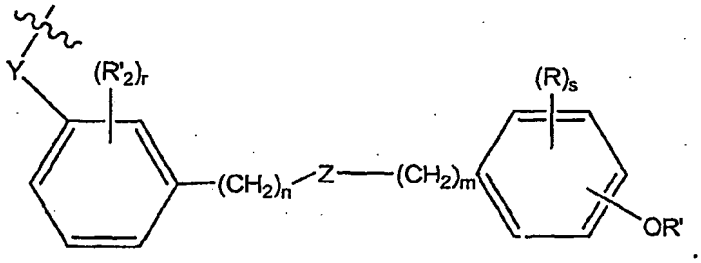


-OH, $-NH_2$, -SH, or . In certain embodiments at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R groups adjacent to -OH are bulky alkyl groups (e.g., butyl, see-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R groups are *tert*-butyl. In another embodiment, both R groups are *tert-bntyl* adjacent to the OH group.

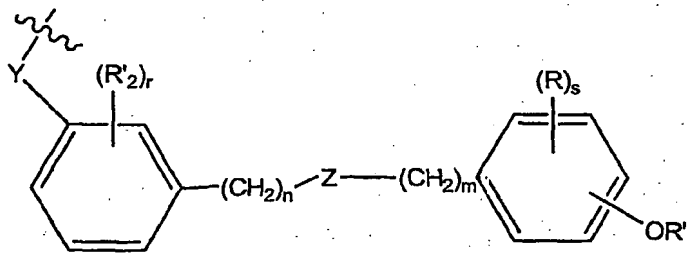
Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. hi certain embodiments at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). hi certain other embodiments both R_1 groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like), hi another embodiment, both R_1 groups are ter/-butyl. In another embodiment, both R_1 groups are *tert*-butyl adjacent to the OH group.

Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,

-OH, -NH_2, -SH or  ,

wherein at least one R_2 is  .

Each R'_2 is independently -M' -X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,

-OH, -NH_2, -SH or  .

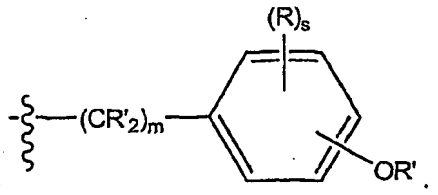
X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -O-, -S-, -NR'- or -C(O)OC(O)-. Optionally an additional value for X is a bond.

Each Y is independently Q-W-Q'.

Each Q is independently an optionally substituted C1-C20 alkylene group.

Each Q' is independently a bond or an optionally substituted C1-C20 alkylene group.

Each W is independently arylene, -0-, -S-, -NR'-, -N(OR')-, -C(=N(0R'))-, -C(O)NR'-, -NR'C(O)-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -C(O)OC(O)-, or a bond.

Each M' is independently -H, alkyl, or  .

Each n and m are independently integers from 0 to 6.

Each s, q and u are independently integers from 0 to 4.

r is an integer from 0 to 4.

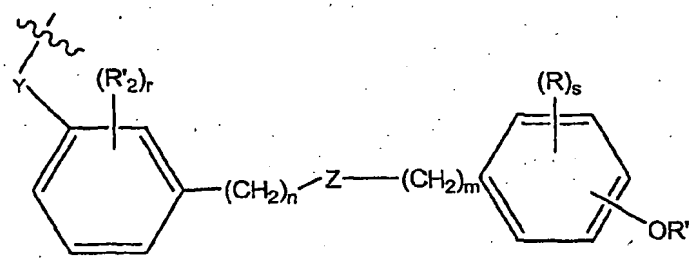
In a second embodiment of the present invention directed to a polymer represented by Structural Formula 2:

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-.

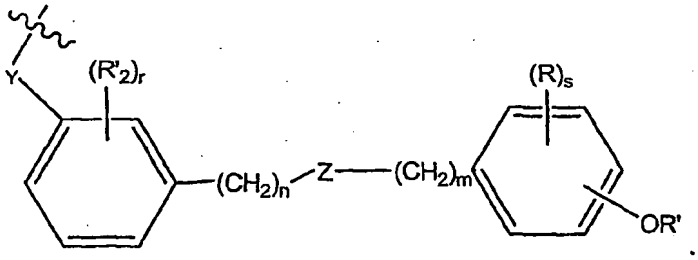
R' is -H.

Each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl.

Each R_2 is independently an optionally substituted alkyl or



wherein one R_2 is:

 .

Each R'_2 is independently -M-X or an optionally substituted alkyl.

Each M' is independently - H or alkyl.

X is -O-.

Each Q is independently an optionally substituted Cl-ClO alkylene group.

Each Q' is independently a bond or an optionally substituted C1-C10 alkylene group.

Each W is independently arylene, -O-, -S-, -NH-, -N(OH)-, -C(=N(OH))-, or a bond.

Each n and m are independently integers from 0 to 2.

Each s and r are independently integers from 0 to 2.

q is an integer from 1 to 3, and the remainder of the variables are as described above in the first embodiment.

In a third embodiment of the present invention directed to a polymer represented by Structural Formula 2:

Z is -C(O)NH- or -NHC(O)-.

Each R is independently an alkyl or an alkoxycarbonyl.

s is 2 and the remainder of the variables are as described above in the second embodiment.

In a fourth embodiment of the present invention directed to a polymer represented by Structural Formula 2:

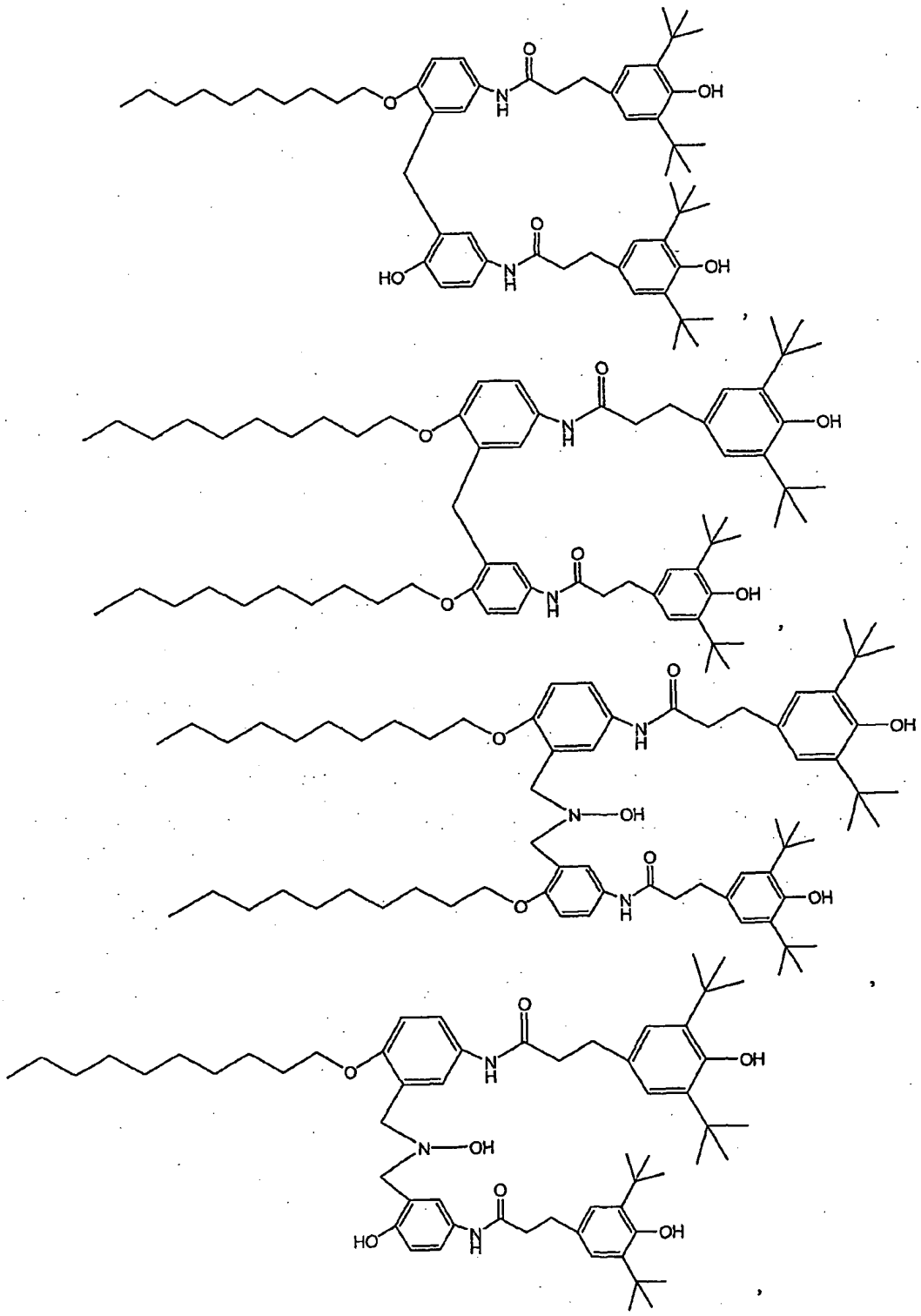
Each R is independently an alkyl group. In certain embodiments R is a bulky alkyl group. In certain embodiments the two R groups are bulky alkyl groups adjacent to the -OH group. In certain embodiments the two R groups are *tert*-butyl groups adjacent to the -OH group.

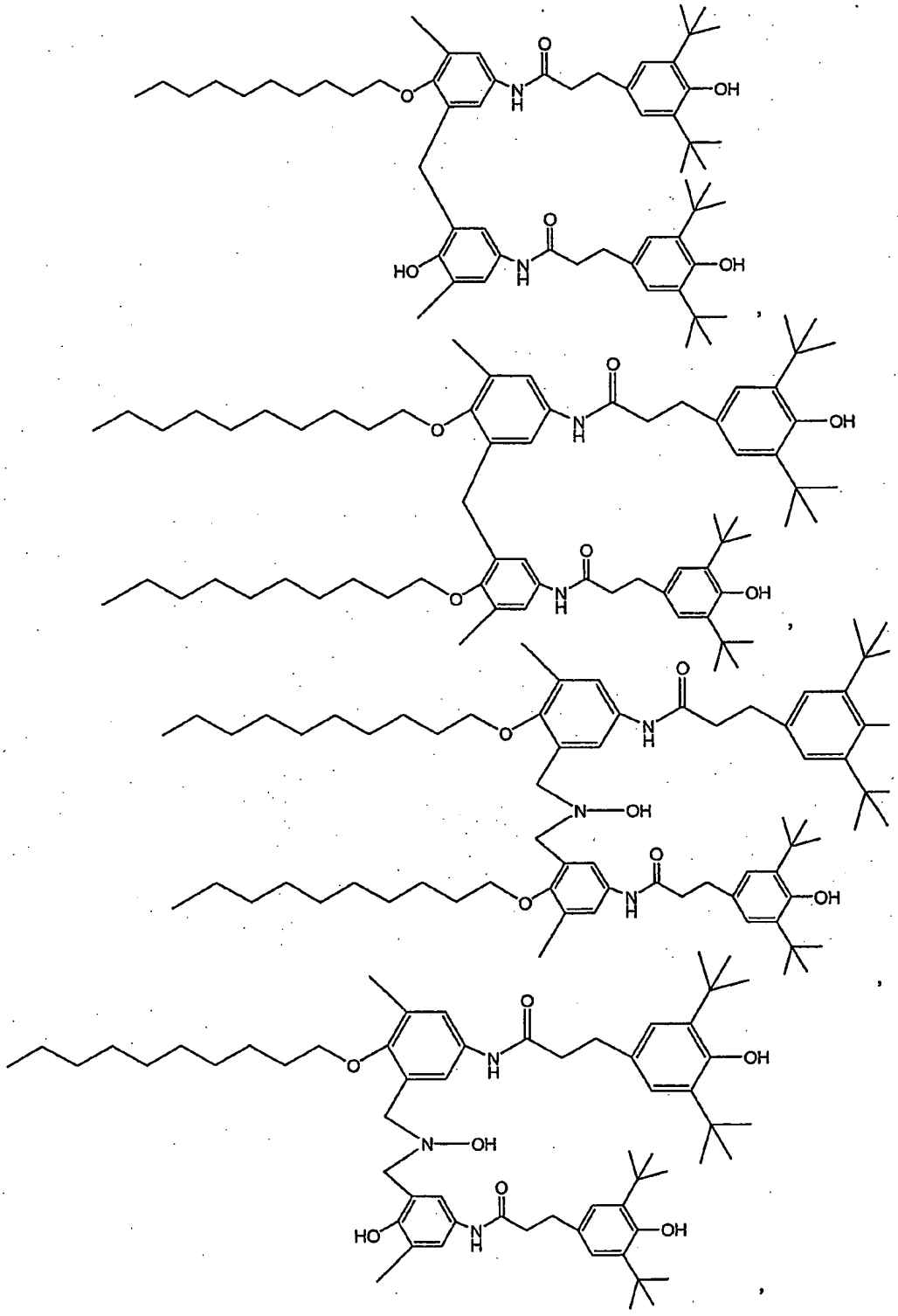
Y is -CR'Y, $-(CR''_2)_p$-phenylene-(CR''_2)p-or-$(CR''_2)_pN(OH)(CR''_2)_p$.

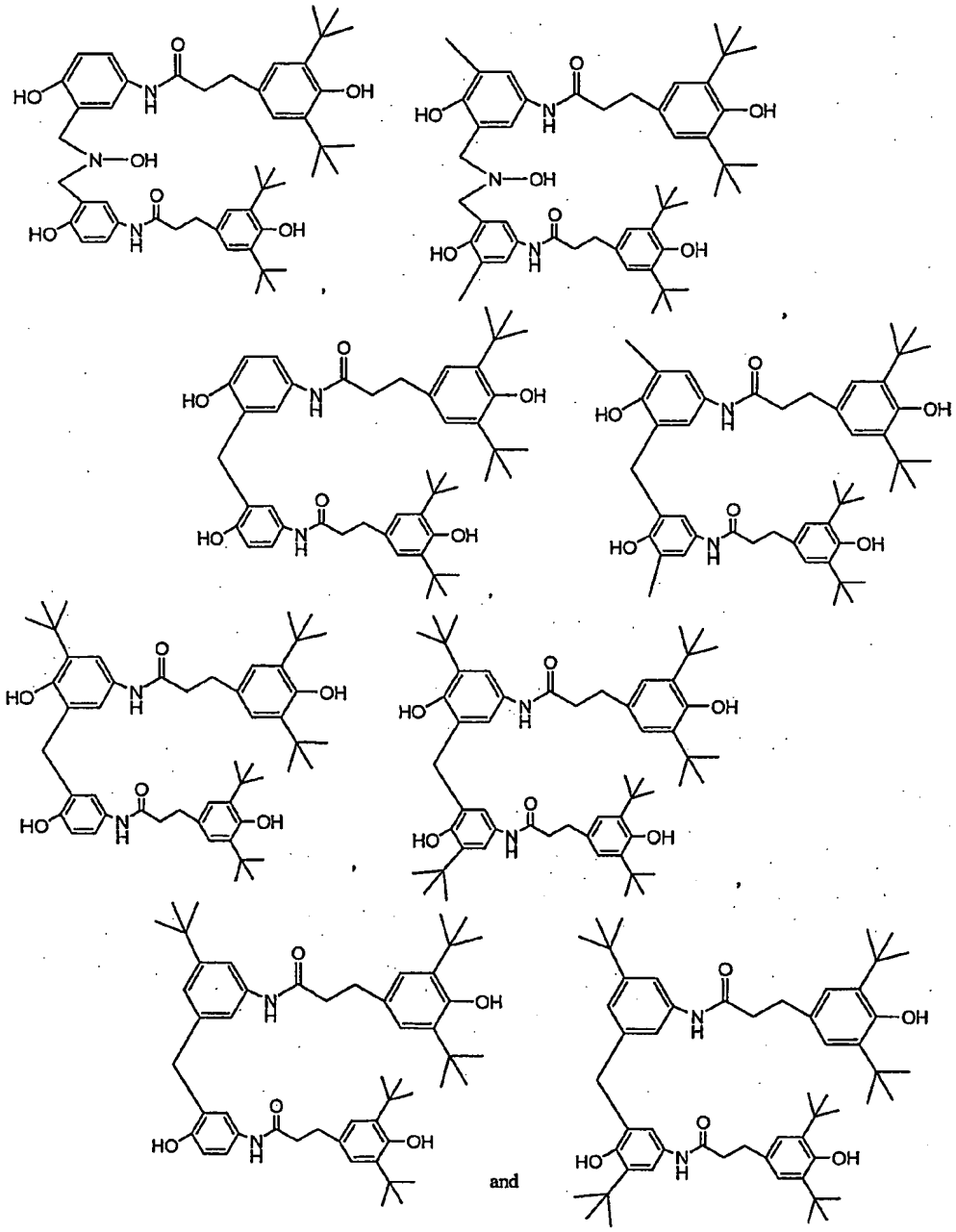
Each R" is - H or alkyl.

Each p is independently an integer of 1 to 5, and the remainder of the variables are as described above in the third embodiment.

In a fifth embodiment of the present invention directed to a polymer represented by Structural Formula 2, the polymer is represented by a Structural Formula selected from:







and

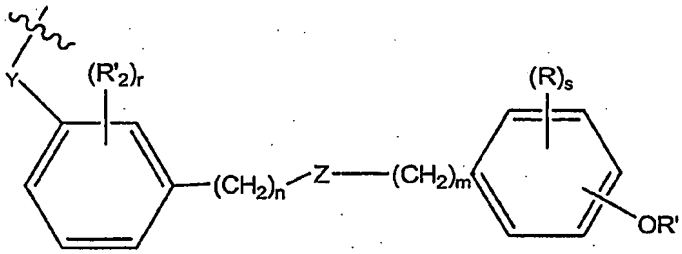
In a sixth embodiment of the present invention directed to a polymer represented by Structural Formula 2:

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-.

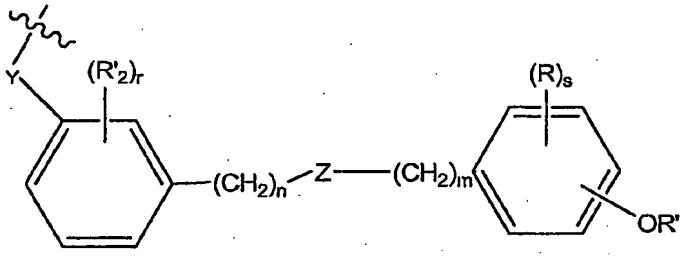
R' is -H.

Each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl.

Each R_2 is independently an optionally substituted alkyl or

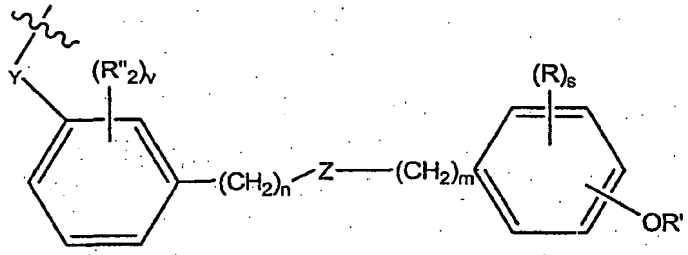


wherein at least one R_2 is

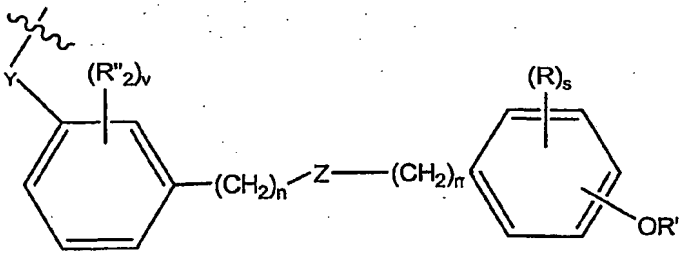


.

Each R'_2 is independently -M'-X, an optionally substituted alkyl or

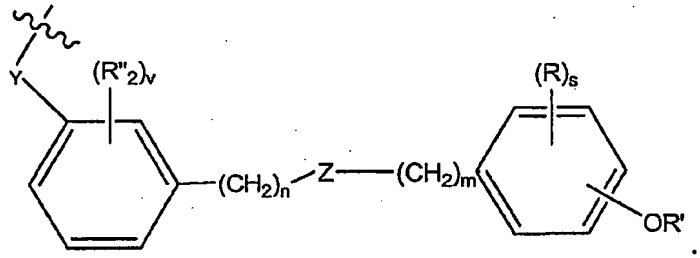


wherein at least one R'_2 is:



.

Each R''_2 is independently -M'-X, an optionally substituted alkyl or



Each M' is independently - H or alkyl.

X is -O-.

Each Q is independently an optionally substituted Cl-ClO alkylene group.

Each Q' is independently a bond or an optionally substituted Cl-ClO alkylene group.

Each W is independently arylene, -O-, -S-, -NH-, -N(OH)-, -C(=N(0H)>, or a bond.

Each n and m are independently integers from 0 to 2.

Each s and v are independently integers from 0 to 2.

Each r and q are independently integers from 1 to 3, and the remainder of the variables are as described above in the first embodiment.

In a seventh embodiment of the present invention directed to a polymer represented by Structural Formula 2:

Z is -C(O)NH- or -NHC(O)-.

Each R is independently an alkyl or an alkoxycarbonyl.

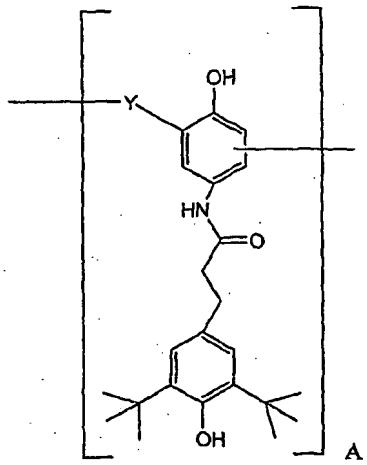
s is 2, and the remainder of the variables are as described above in the sixth embodiment.

In an eighth embodiment of the present invention directed to a polymer represented by Structural Formula 2:

Each R is independently an alkyl group and the remainder of the variables are as described above in the seventh embodiment. In certain embodiments R is a bulky alkyl group. In certain embodiments the two R groups are bulky alkyl groups

adjacent to the -OH group. In certain embodiments the two R groups are ter/-butyl groups adjacent to the -OH group.

In a ninth embodiment of the present invention directed to a polymer represented by Structural Formula 2 the polymer comprises a repeat unit represented by the following Structural Formula:



A is an integer of 3 or greater.

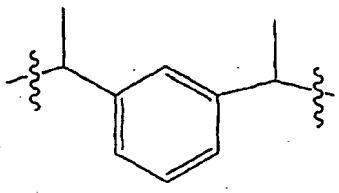
Y is -CR'V, -(CR" $_2$)p-phenylene-(CR" $_2$)p-or-(CR" $_2$)pN(OH)(CR"2)p.

Each R" is - H or alkyl. In certain embodiments R" is a linear or branched Cl-ClO alkyl.

Each p is independently an integer of 1 to 5, and the remainder of the variables are as described above in the eighth embodiment.

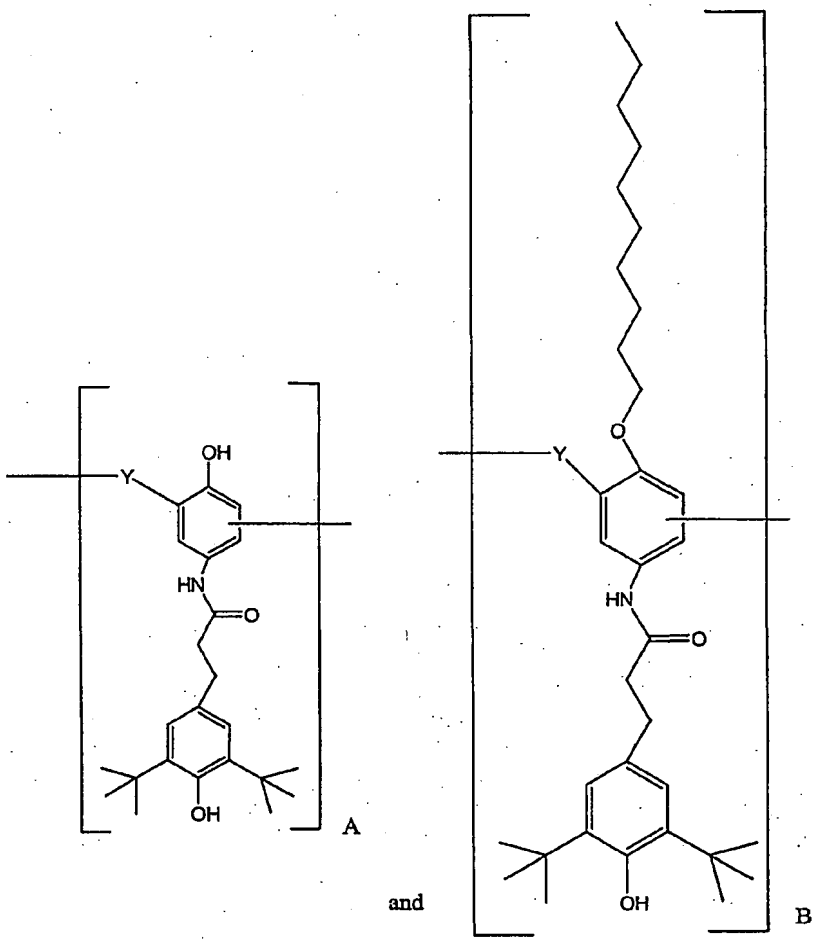
In a tenth embodiment of the present invention directed to a polymer represented by Structural Formula 2:

Y is -CH $_2$, -$CH_2N(OH)CH_2$- or



and the remainder of the variables are as described above in the ninth embodiment.

In an eleventh embodiment of the present invention directed to a polymer represented by Structural Formula 2 the polymer comprises repeat units represented by the following Structural Formulas:



A and B are integers of 1 or greater and the sum of A and B is 3 or greater.

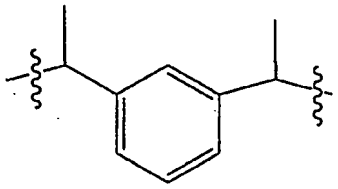
Y is -CR' V , -$(CR''_2)_p$-phenylene-$(CR''_2)_p$-or -$(CR''_2)_pN(OH)(CR''_2)_p$.

Each R" is - H or alkyl.

Each p is independently an integer of 1 to 5, and the remainder of the variables are as described above in the eighth embodiment.

In a twelfth embodiment of the present invention directed to a polymer represented by Structural Formula 2:

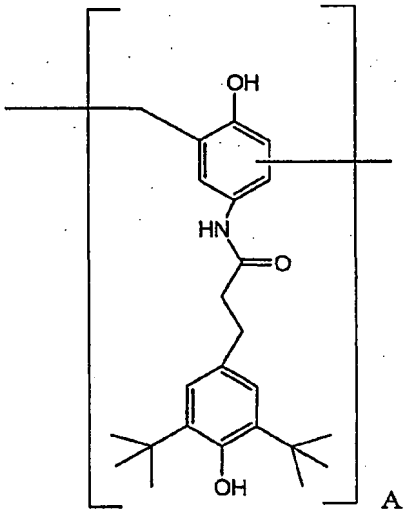
Y is -CH_2, -$CH_2N(OH)CH_2$- or



and the remainder of the variables are as described above in the eleventh embodiment.

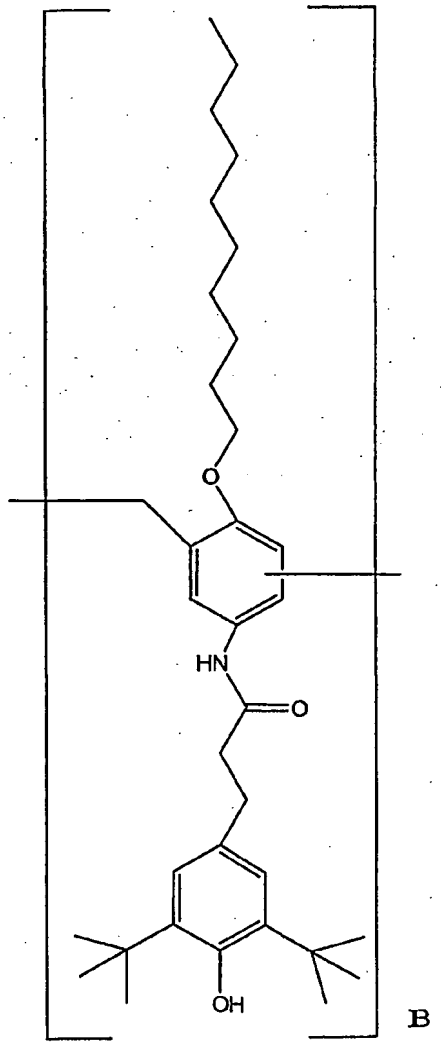
In certain embodiments the molar ratios of A:B are 1:1, 1:2, 1:3, 1:4, 1: or 1:10. In certain embodiments the molar ratios are 1: 1 or 1:2.

In an thirteenth embodiment of the present invention directed to a polymer represented by Structural Formula 2 the polymer comprises repeat units represented by the following Structural Formulas:



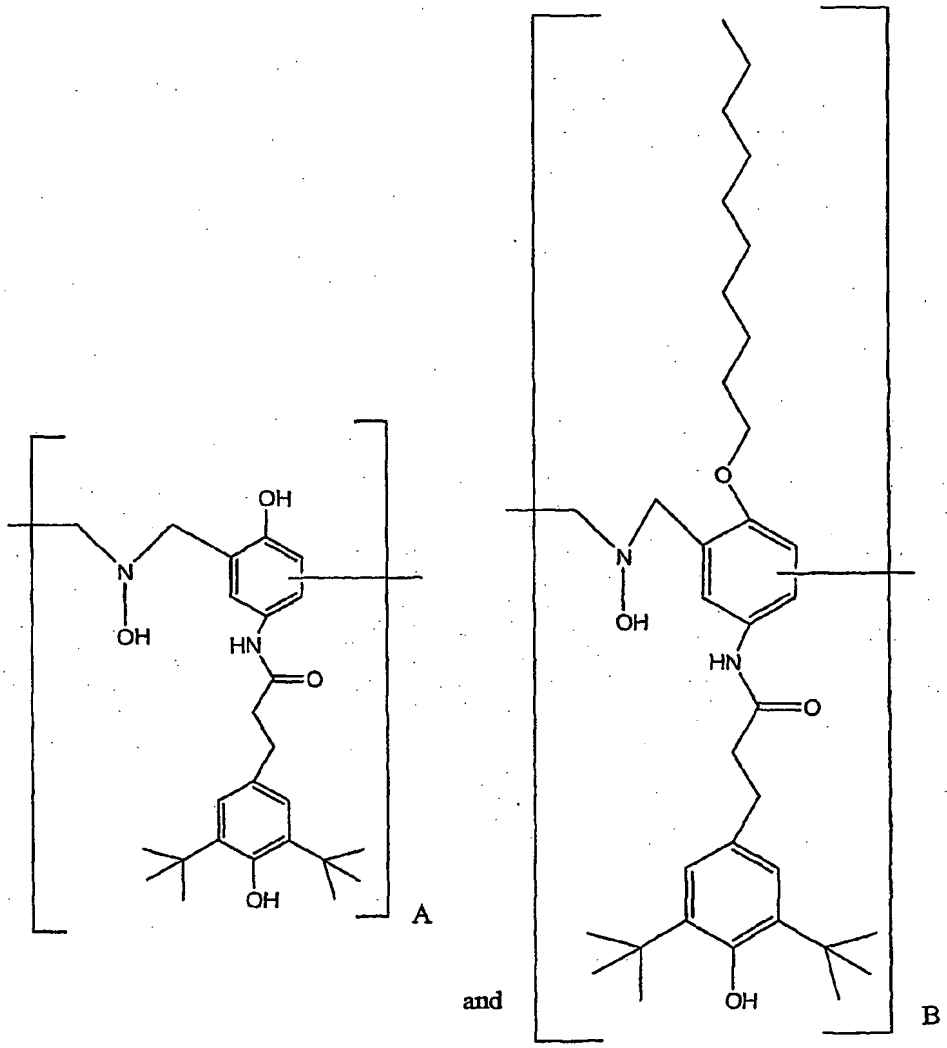
A

and



B

In an fourteenth embodiment of the present invention directed to a polymer represented by Structural Formula 2 the polymer comprises repeat units represented by the following Structural Formulas:



In certain embodiments, it is understood that where a repeat unit forms the end of a polymer chain the linking group Y is not present. In certain embodiments when a repeat unit form the end of a polymer chain the linking group Y can be replaced by an alkyl group such a methyl, ethyl, *tert*-butyl etc., i.e., an alkyl group which is *meta* to where the phenyl ring joins the rest of the molecule.

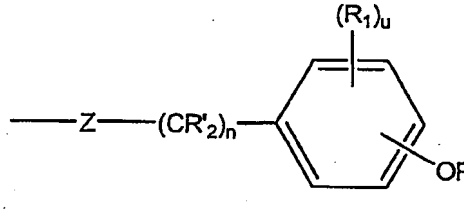
In another embodiment the present invention is directed to a composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3.

In a first embodiment for the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3:

Each Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond.

Each R' is independently -H or optionally substituted alkyl.

Each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester,

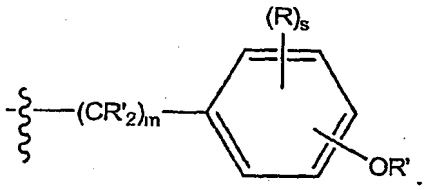


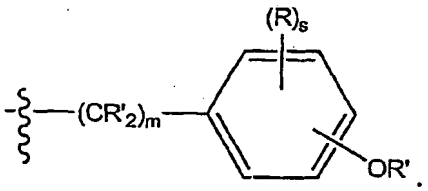
-OH, $-NH_2$, -SH, or . certain embodiments at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R groups are *tert*-butyl. In another embodiment, both R groups are *tert*-butyl adjacent to the OH group.

Each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH. In certain embodiments at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In certain other embodiments both R_1 groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R_1 groups are *tert*-butyl. In another embodiment, both R_1 groups are *tert*-butyl adjacent to the OH group.

Each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH.

Each X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-. Optionally an additional values for X is a bond.

M is an alkyl or 

M' is a -H, alkyl or 

Each n and m are independently integers from Oto 6.

Each s, q and u are independently integers from Oto 4.

In a second embodiment for the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3:

Each Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-.

R' is -H.

Each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl.

Each R_2 is independently an optionally substituted alkyl.

X is -0-.

M is an alkyl. In certain embodiments M is a C1-C20 alkyl.

M' is - H or alkyl. In certain embodiments M' is - H or C1-C20 alkyl.

Each n and m are independently integers from Oto 2.

Each s and q are independently integers from Oto 2, and the remainder of the variables are as described above for the first embodiment.

In a third embodiment for the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3:

Z is -C(O)NH- or -NHC(O)-.

Each R is independently an alkyl or an alkoxycarbonyl.

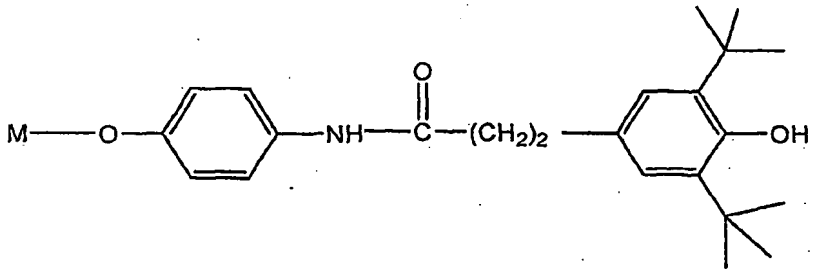
Each R_2 is independently an alkyl.

s is *2*, and the remainder of the variables are as described above for the second embodiment.

In a fourth embodiment for the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3:

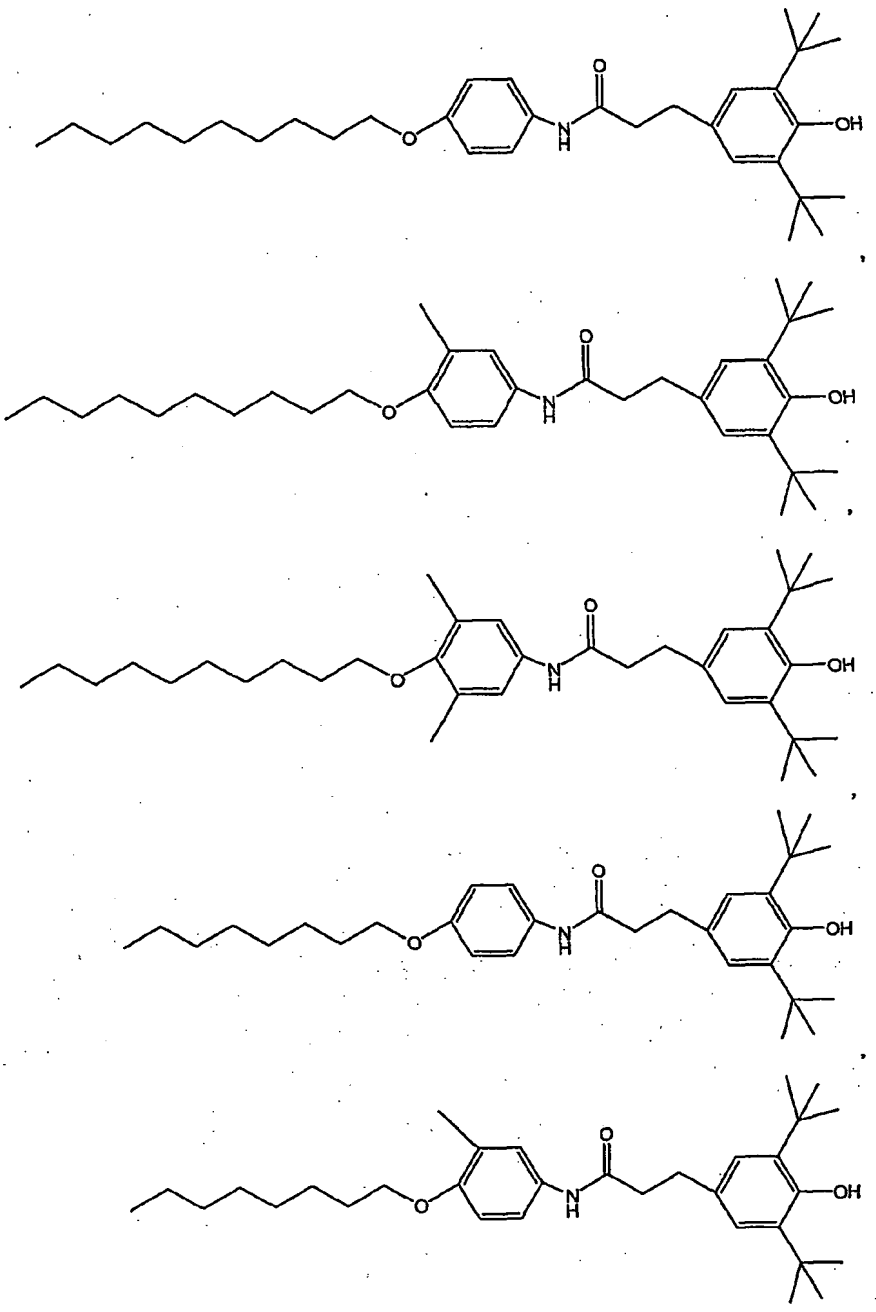
Each R is independently an alkyl group, and the remainder of the variables are as described above for the third embodiment. In certain embodiments R is a bulky alkyl group. In certain embodiments the two R groups are bulky alkyl groups adjacent to the —OH group. In certain embodiments the two R groups are *tert*-butyl groups adjacent to the —OH group.

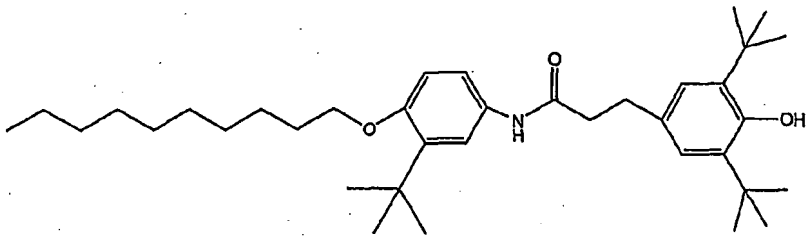
In a fifth embodiment for the composition comprising a compound represented by Structural Formula 1 as described above and a compound represented by Structural Formula 3 the compound represented by Structural Formula 1 is represented by the following Structural Formula:

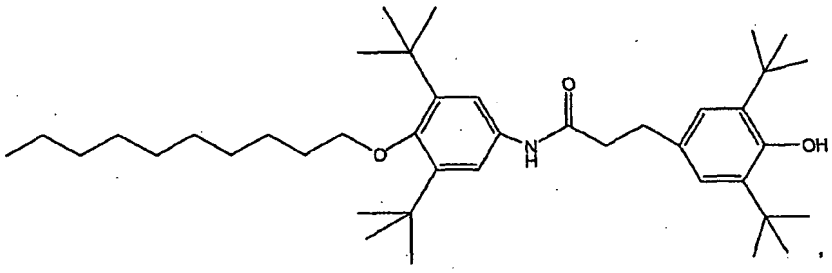


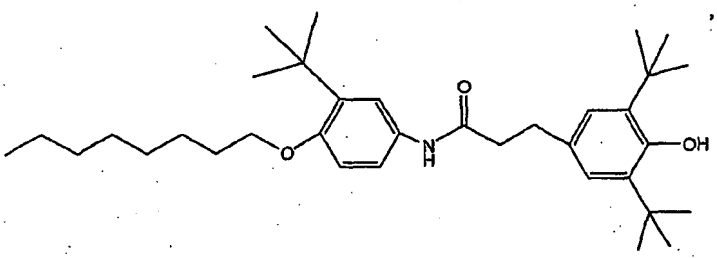
M is a C1 to C20 linear or branched alkyl chain, and the remainder of the variables are as described above for the fourth embodiment.

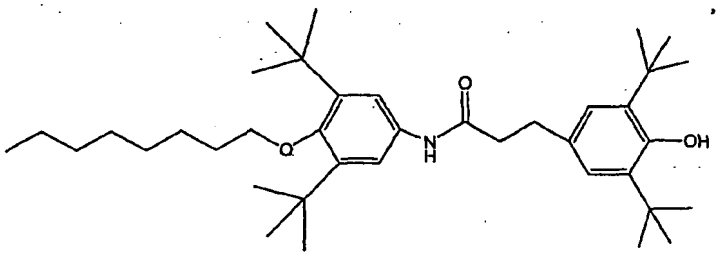
In a sixth embodiment for the composition comprising a compound represented by Structural Formula 1 as described above and a compound represented by Structural Formula 3 the compound represented by Structural Formula 1 is represented a Structural Formula selected from:

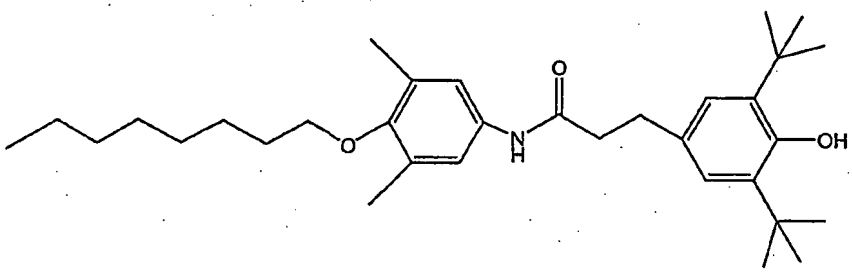


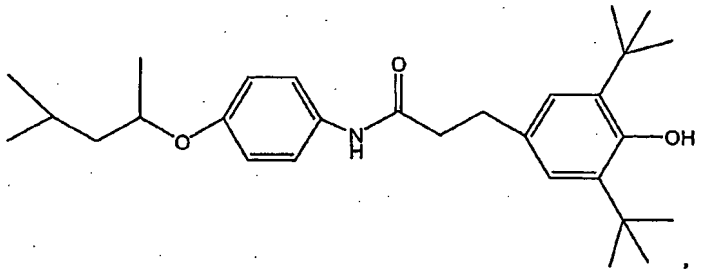


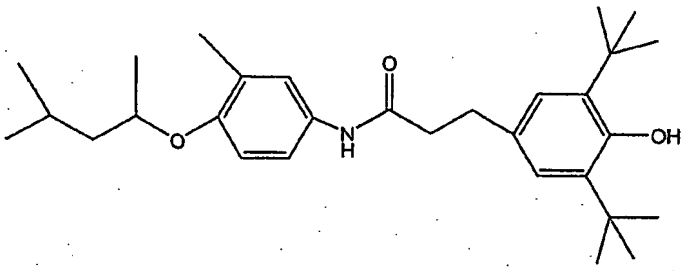




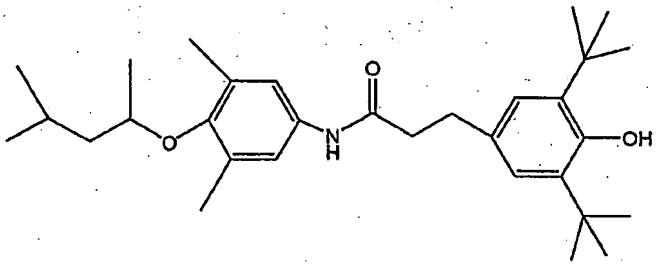




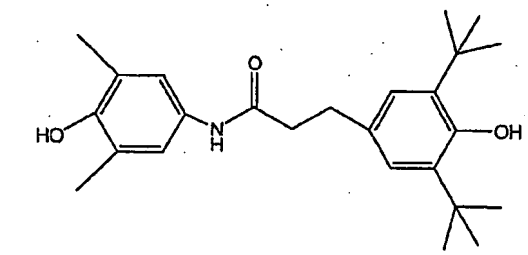


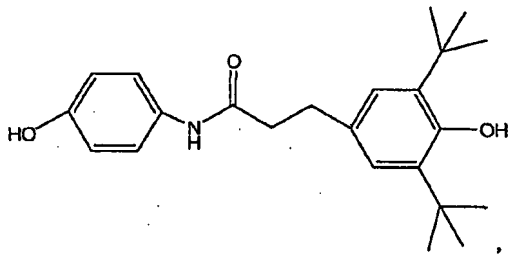


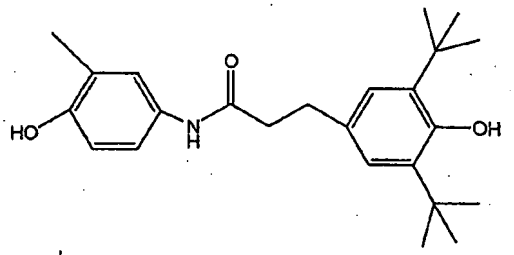
or

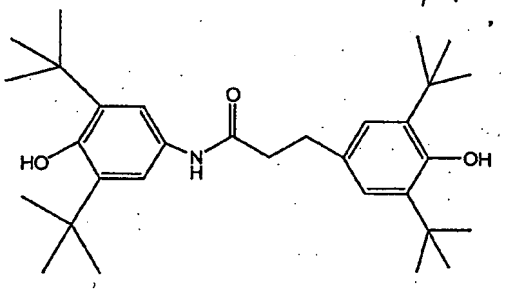


In a seventh embodiment for the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3 the compound represented by Structural Formula 3 is represented a Structural Formula selected from:

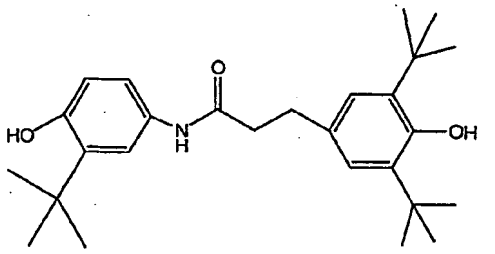








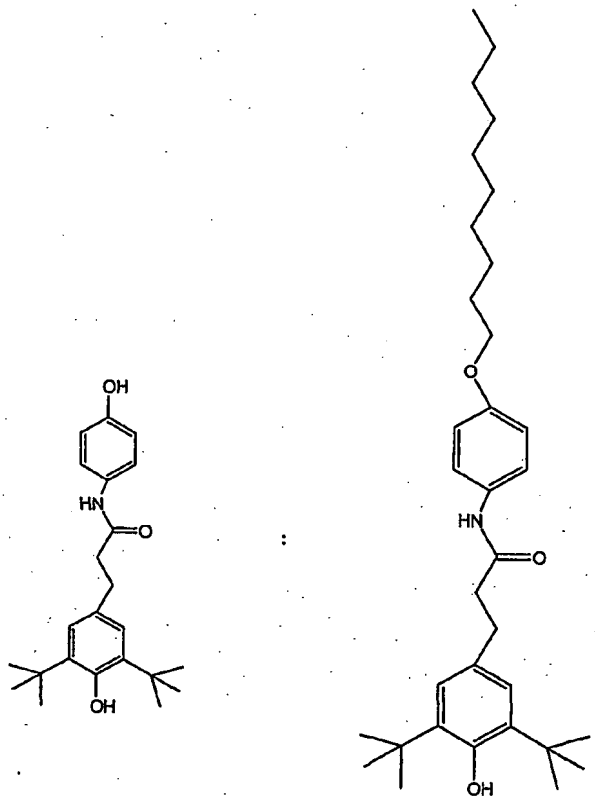
or



In an eighth embodiment for the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3 the weightweight ratio of compound lrcompound 3 is 1:1, 1:2, 1:3, 1:5 or 1:10.

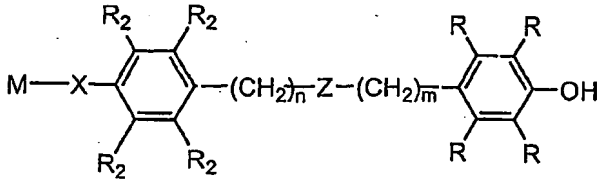
In an eighth embodiment for the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3 the weightweight ratio of compound 1:compound 3 is 1:2.

In a ninth embodiment of the present invention the composition comprising a compound represented by Structural Formula 1 and a compound represented by Structural Formula 3 is represented as follows:



1 : 2

In particular, the present invention pertains to novel and effective alkylated antioxidant macromolecules having formula I:



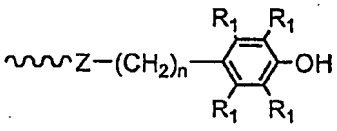
I

wherein, independently for each occurrence,

n and m are integers from Oto 6, inclusive;

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -CH=N-, -C(O)-, -O-, -S-, -C(O)OC(O)-, or a bond;

R is H, C_{1-6} alkyl, -OH, $-NH_2$, -SH, aryl, ester, or



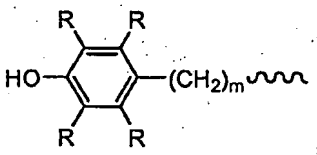
, wherein at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like);

R_1 is H, C_{1-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or C1-C6 alkyl ester wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like); and

R_2 is H, C_{1-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or ester, wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like);

X is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -CH=N-, -C(O)-, -O-, -S-, -C(O)OC(O)-, or a bond;

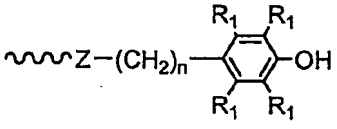
M is H, aryl, C-I to C-20 linear or branched alkyl chain with or without any functional group anywhere in the chain, or



, wherein m and each R is independently as described above;

wherein

R_2 is H, C_{1-6} alkyl, -OH, $-NH_2$, -SH, aryl, ester, or

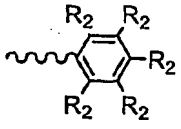


, wherein at least one R_2 is -OH and n, Z, and each R1 are independently as described above.

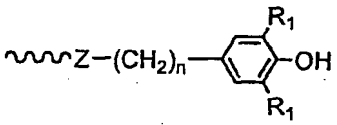
In various embodiments, the present invention relates to a compound of formula I and the attendant definitions, wherein Z is -OC(O)-. In another embodiment, Z is -C(O)O-. In another embodiment, Z is -C(O)NH-. In another embodiment, Z is -NHC(O)-. In another embodiment, Z is -NH-. In another

embodiment, Z is -CH=N-. In another embodiment, Z is -C(O)-. In another embodiment, Z is -O-. In another embodiment, Z is -C(O)OC(O)-. In another embodiment, Z is a bond.

In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein both R groups adjacent to -OH are bulky alkyl groups (e.g., butyl, sec-butyl, *tert-butyl,* 2-propyl, 1,1-dimethylhexyl, and the like). In another embodiment, both R groups are *tert*-butyl.

In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein M is  .

In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein at least one R is



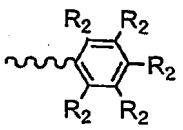
In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0.

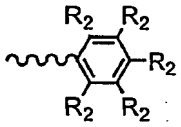
In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein m is 1.

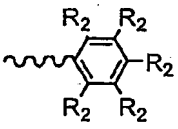
In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0 and m is 1.

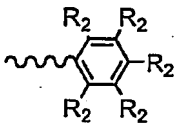
In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0, m is 1, and Z is -C(O)O-.

In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0, m is 1, Z is -C(O)O-, and the two R groups adjacent to the OH are *tert*-butyl.

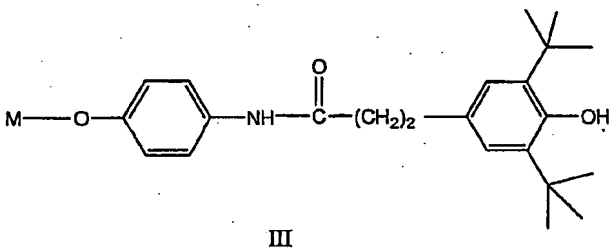
In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0, m is 1, Z is -C(O)O-, the two R groups adjacent to the OH are t-butyl, and M is  .

In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0, m is 1, Z is -C(O)O-, the two R groups adjacent to the OH are t-butyl, M is  , and the R_2 in the para position is OH.

In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0, m is 1, Z is -C(O)O-, the two R groups adjacent to the OH are t-butyl, M is  , the R_2 in the para position is OH, and an adjacent R_2 is OH.

In another embodiment, the present invention relates to a compound of formula I and the attendant definitions, wherein n is 0, m is 1, Z is -C(O)O-, the two R groups adjacent to the OH are t-butyl, M is  , the R_2 in the para position is OH, and the two adjacent R_2 groups are -OH.

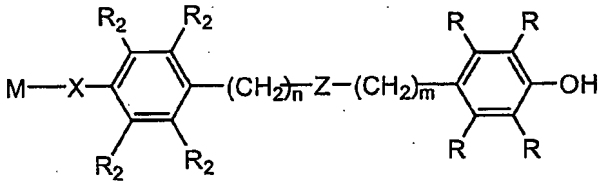
In some embodiments, the present invention relates to compounds that are alkylated macromolecular antioxidants of the formula III.



III

where M is C1 to C20- linear or branched alkyl chains. The compounds of formula III can have antioxidant properties.

In certain embodiments the present invention relates to a compound represented by Structural Formula I:

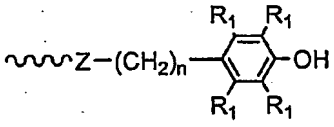


I

wherein, independently for each occurrence,

n and m are integers from 0 to 6, inclusive;

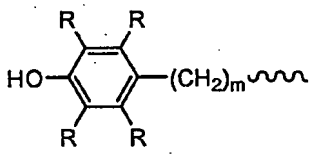
Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -CH=N-, -C(O)-, -0-, -S-, -C(O)OC(O)-, or a bond;

R is H, C_{1-6} alkyl, -OH, $-NH_2$, -SH, aryl, ester, or  , wherein at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like);

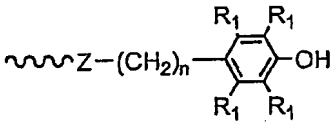
R_1 is H, C_{1-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or C1-C6 alkyl ester wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like); and

R_2 is H, C_{1-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or ester, wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like);

X is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -CH=N-, -C(O)-, -O-, -S-, -C(O)OC(O)-, or a bond;

M is H, aryl, C-I to C-20 linear or branched alkyl chain with or without any functional group anywhere in the chain, or  , wherein m and each R is independently as described above;

wherein



R_2 is H, C_{1-6} alkyl, -OH, $-NH_2$, -SH, aryl, ester, or , wherein at least one R_2 is -OH and n, Z, and each R1 are independently as described above.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -OC(O)-.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is C(O)O-.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -C(O)NH-.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -NHC(O)-.

hi certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -NH-.

hi certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -CH=N-.

Li certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -C(O)-.

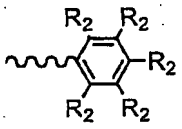
In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -0-.

hi certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -C(O)OC(O)-.

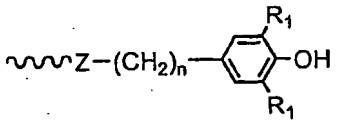
In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is a bond.

hi certain embodiments the present invention relates to a compound represented by Structural Formula I wherein the R groups adjacent to -OH are both bulky alkyl groups.

hi certain embodiments the present invention relates to a compound represented by Structural Formula I wherein the R groups adjacent to -OH are both *tert-butyl.*

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein M is  .

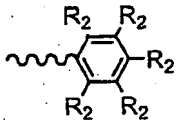
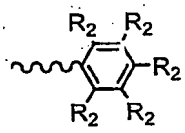
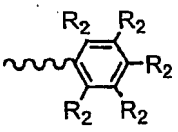
In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein at least one R is



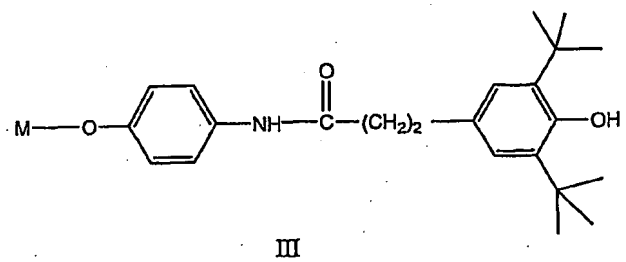
In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein n is 0.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein m is 1.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein n is 0.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein Z is -C(O)O-, wherein the R groups adjacent to -OH are both *tert-bntyl,* wherein M is  , wherein the R_2 in the para position of the  represented by M is -OH, wherein the R_2 adjacent to the R_2 in the para position of the  represented by M are -OH.

In certain embodiments the present invention relates to a compound represented by Structural Formula I wherein the compound is represented by Structural Formula III:



III

where M is a C1 to C20- linear or branched alkyl chain.

The term "alkyl" as used herein means a saturated straight-chain, branched or cyclic hydrocarbon. When straight-chained or branched, an alkyl group is typically C1-C20, more typically Cl-ClO; when cyclic, an alkyl group is typically C3-C12, more typically C3-C7. Examples of alkyl groups include methyl, ethyl, M-propyl, wo-propyl, rø-butyl, sec-butyl and *t*ert-butyl and 1,1-dimethylhexyl.

The term "alkoxy" as used herein is represented by -OR**, wherein R** is an alkyl group as defined above.

The term "carbonyl" as used herein is represented by -C(=O)R**, wherein R** is an alkyl group as defined above.

The term "alkoxycarbonyl" as used herein is represented by -C(^=O)OR**, wherein R** is an alkyl group as defined above.

The term "aromatic group" includes carbocyclic aromatic rings and heteroaryl rings. The term "aromatic group" may be used interchangeably with the terms "aryl", "aryl ring" "aromatic ring", "aryl group" and "aromatic group".

Carbocyclic aromatic ring groups have only carbon ring atoms (typically six to fourteen) and include monocyclic aromatic rings such as phenyl and fused polycyclic aromatic ring systems in which a carbocyclic aromatic ring is fused to one or more aromatic rings (carbocyclic aromatic or heteroaromatic). Examples include 1-naphthyl, 2-naphthyl, 1-anthracyl and 2-anthracyl. Also included within the scope of the term "carbocyclic aromatic ring", as it is used herein, is a group in which an aromatic ring is fused to one or more non-aromatic rings (carbocyclic or heterocyclic), such as in an indanyl, phthalimidyl, naphthimidyl, phenanthridinyl, or tetrahydronaphthyl.

The term "heteroaryl", "heteroaromatic", "heteroaryl ring", "heteroaryl group" and "heteroaromatic group", used alone or as part of a larger moiety as in "heteroaralkyl" refers to heteroaromatic ring groups having five to fourteen

members, including monocyclic heteroaromatic rings and polycyclic aromatic rings in which a monocyclic aromatic ring is fused to one or more other aromatic ring (carbocyclic or heterocyclic). Heteroaryl groups have one or more ring heteroatoms. Examples of heteroaryl groups include 2-furanyl, 3-furanyl, iV-imidazolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, oxadiazolyl, oxadiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, *N*-pyrazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, iV-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 3-pyridazinyl, *A*-pyridazinyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, triazolyl, tetrazolyl, 2-thienyl, 3-thienyl, carbazolyl, benzothienyl, benzofuranyl, indolyl, quinolinyl, benzothiazole, benzooxazole, benzimidazolyl, isoquinolinyl and isoindolyl. Also included within the scope of the term "heteroaryl", as it is used herein, is a group in which an aromatic ring is fused to one or more non-aromatic rings (carbocyclic or heterocyclic).

An "arylene" group as defined herein is a bivalent group represented by -Ar-, wherein Ar is an aromatic group as defined above.

The term non-aromatic heterocyclic group used alone or as part of a larger moiety refers to non-aromatic heterocyclic ring groups having three to fourteen members, including monocyclic heterocyclic rings and polycyclic rings in which a monocyclic ring is fused to one or more other non-aromatic carbocyclic or heterocyclic ring or aromatic ring (carbocyclic or heterocyclic). Heterocyclic groups have one or more ring heteroatoms, and can be saturated or contain one or more units of unsaturation. Examples of heterocyclic groups include piperidinyl, piperizinyl, pyrrolidinyl, pyrazolidinyl, imidazolidinyl, tetrahydroquinolinyl, inodolinyl, isoindolinyl, tetrahydrofuranyl, oxazolidinyl, thiazolidinyl, dioxolanyl, dithiolanyl, tetrahydropyranyl, dihydropyranyl, azepanyl and azetidinyl

The term "heteroatom" means nitrogen, oxygen, or sulfur and includes any oxidized form of nitrogen and sulfur, and the quaternized form of any basic nitrogen. Also the term "nitrogen" includes a substitutable nitrogen of a heteroaryl or non-aromatic heterocyclic group. As an example, in a saturated or partially unsaturated ring having 0-3 heteroatoms selected from oxygen, sulfur or nitrogen, the nitrogen may be N (as in 3,4-dihydro-2/f-pyrrolyl), NH (as in pyrrolidinyl) or NR" (as in N-

substituted pyrrolidinyl), wherein R" is a suitable substituent for the nitrogen atom in the ring of a non-aromatic nitrogen-containing heterocyclic group, as defined below. Preferably the nitrogen is unsubstituted.

As used herein the term non-aromatic carbocyclic ring as used alone or as part of a larger moiety refers to a non-aromatic carbon containing ring which can be saturated or contain one or more units of unsaturation, having three to fourteen atoms including monocyclic and polycyclic rings in which the carbocyclic ring can be fused to one or more non-aromatic carbocyclic or heterocyclic rings or one or more aromatic (carbocyclic or heterocyclic) rings

An optionally substituted aryl group as defined herein may contain one or more substitutable ring atoms, such as carbon or nitrogen ring atoms. Examples of suitable substituents on a substitutable ring carbon atom of an aryl group include halogen (e.g., -Br, Cl, I and F), -OH, C1-C4 alkyl, C1-C4 haloalkyl, $-NO_2$, C1-C4 alkoxy, C1-C4 haloalkoxy, -CN, $-NH_2$, C1-C4 alkylamino, C1-C4 dialkylamino, $-C(O)NH_2$, -C(O)NH(C1-C4 alkyl), -C(O)(C1-C4 alkyl), -OC(O)(C1-C4 alkyl), -OC(O)(aryl), -OC(O)(substituted aryl), -OC(O)(aralkyl), -OC(O)(substituted aralkyl), -NHC(O)H, -NHC(O)(C1-C4 alkyl), $-C(O)N(C1\text{-}C4\ alkyl)_2$, -NHC(O)O-(C1-C4 alkyl), -C(O)OH, -C(O)O-(C1-C4 alkyl), $-NHC(O)NH_2$, -NHC(O)NH(C1-C4 alkyl), $-NHC(O)N(C1\text{-}C4\ alkyl)_2$, $-NH\text{-}C(=NH)NH_2$, $-SO_2NH_2$ $-SO_2NH$(C1-C3alkyl), $-SO_2N(C1\text{-}C3alkyl)_2$, $NHSO_2H$, $NHSO_2$(C1-C4 alkyl) and aryl. Preferred substituents on aryl groups are as defined throughout the specification. In certain embodiments aryl groups are unsubstituted.

Examples of suitable substituents on a substitutable ring nitrogen atom of an aryl group include C1-C4 alkyl, NH_2, C1-C4 alkylamino, C1-C4 dialkylamino, $-C(O)NH_2$, -C(O)NH(C1-C4 alkyl), -C(O)(C1-C4 alkyl), $-CO_2R^{**}$, $-C(O)C(O)R^{**}$, $-C(O)CH_3$, -C(O)OH, -C(O)O-(C1-C4 alkyl), $-SO_2NH_2$ $-SO_2NH$(C1-C3alkyl), $-SO_2N(C1\text{-}C3alkyl)_2$, $NHSO_2H$, $NHSO_2$(C1-C4 alkyl), $-C(=S)NH_2$, -C(=S)NH(C1-C4 alkyl), $-C(=S)N(C1\text{-}C4\ alkyl)_2$, $-C(=NH)\text{-}N(H)_2$, -C(=NH)-NH(C1-C4 alkyl) and $-C(=NH)\text{-}N(C1\text{-}C4\ alkyl)_2$,

An optionally substituted alkyl group or non-aromatic carbocyclic or heterocyclic group as defined herein may contain one or more substituents. Examples of suitable substituents for an alkyl group include those listed above for a

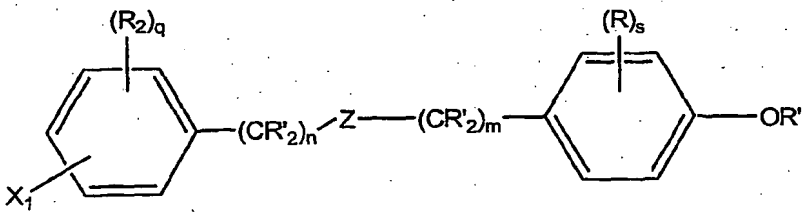
substitutable carbon of an aryl and the following: =0, =S, ==NNHR**, $=NN(R^{**})_2$, $=NNHC(O)R^{**}$, $=NNHCO_2$ (alkyl), $=NNHSO_2$ (alkyl), =NR**, spiro cycloalkyl group or fused cycloalkyl group. R** in each occurrence, independently is -H or C1-C6 alkyl. Preferred substituents on alkyl groups are as defined throughout the specification. In certain embodiments optionally substituted alkyl groups are unsubstituted.

A "spiro cycloalkyl" group is a cycloalkyl group which shares one ring carbon atom with a carbon atom in an alkylene group or alkyl group, wherein the carbon atom being shared in the alkyl group is not a terminal carbon atom.

hi yet another embodiment, the present invention is a method of producing a compound or a polymer described herein using methods know in the art of organic and polymer chemistry.

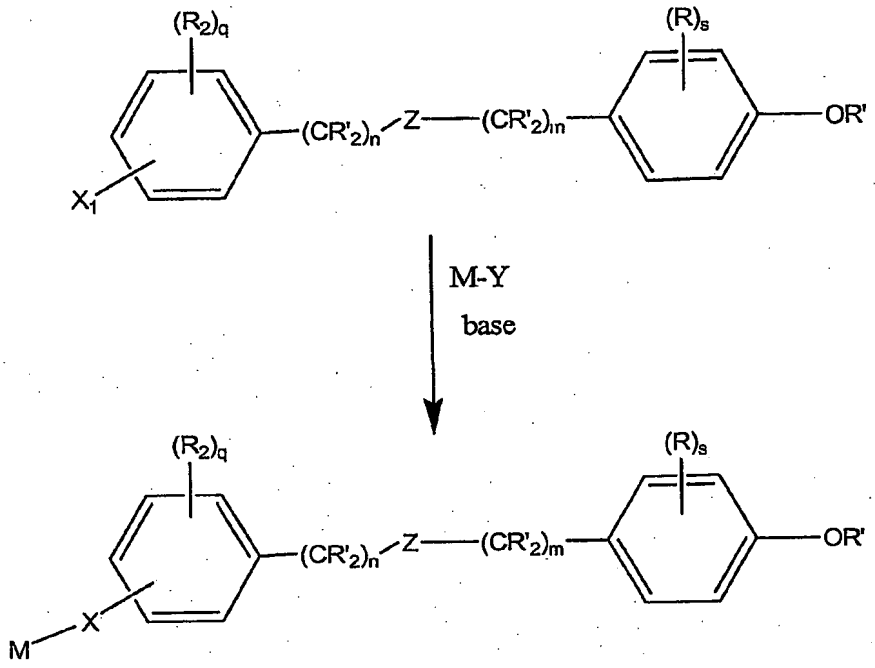
hi certain embodiments this invention can allow synthesizing macromolecular antioxidants cost effectively. In these embodiments these methods also reports an improved, highly efficient and economical process for the synthesis of alkylated macromolecular antioxidants.

hi various embodiments, the alkylated macromolecular antioxidants of the present invention can be prepared by the modification of compounds represented by the following Structural Formula:



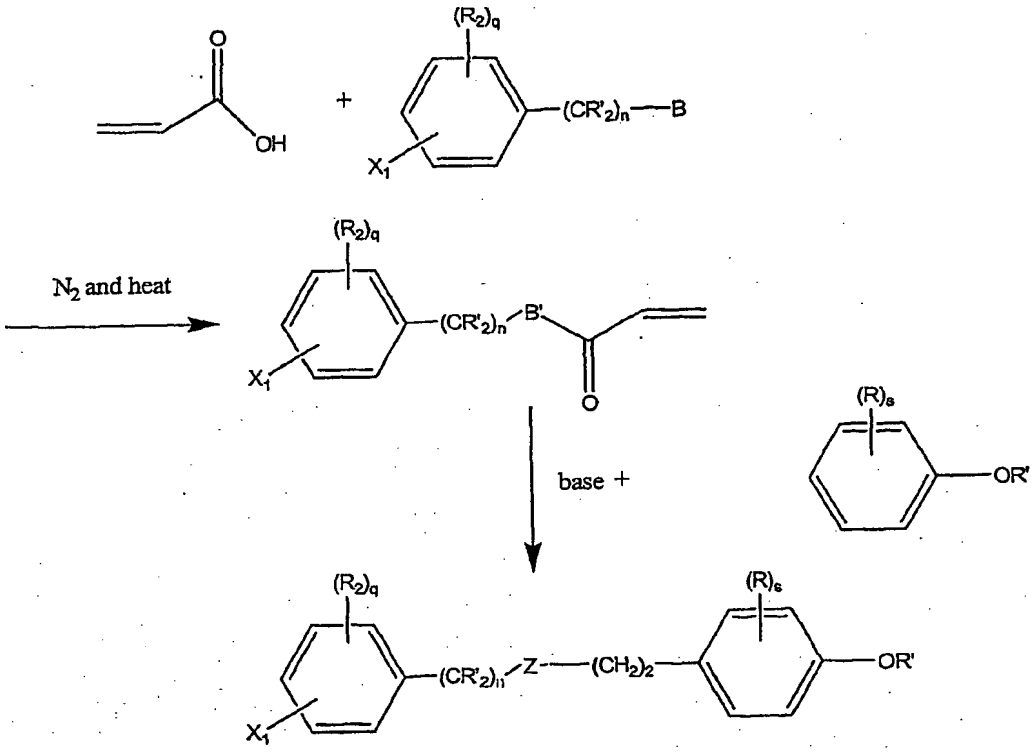
wherein X_1 is -C(O)OH, -OH, $-NH_2$ or -SH and the remainder of the variables are as described above.

In various embodiments, the alkylated macromolecular antioxidants of the present invention can be prepared as shown in the following Scheme:



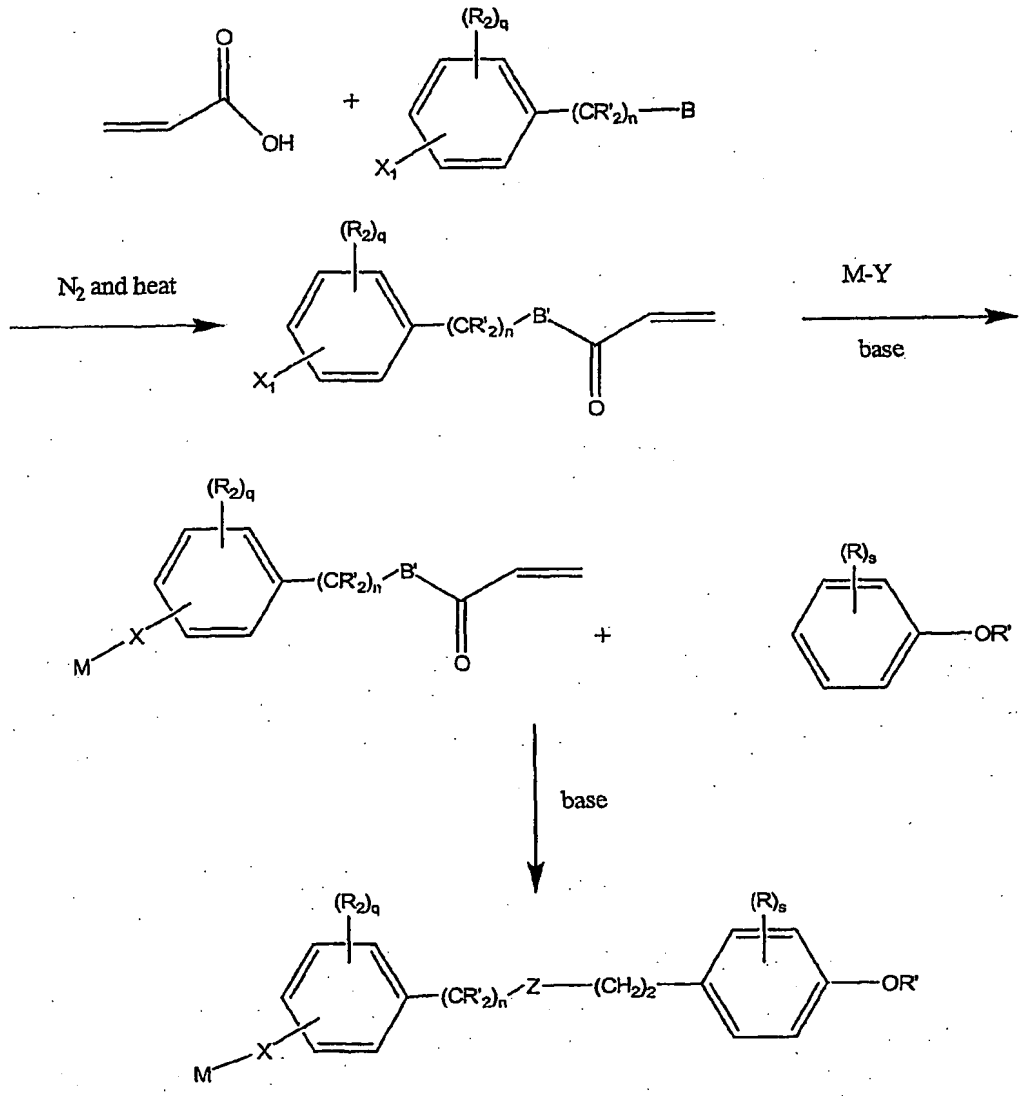
where Y is halogen (Cl, Br, or I) and M-Y can be dimethyl sulphate and the remainder of the variables are as described above.

In various embodiments, the alkylated macromolecular antioxidants of the present invention can be prepared as shown in the following Scheme:



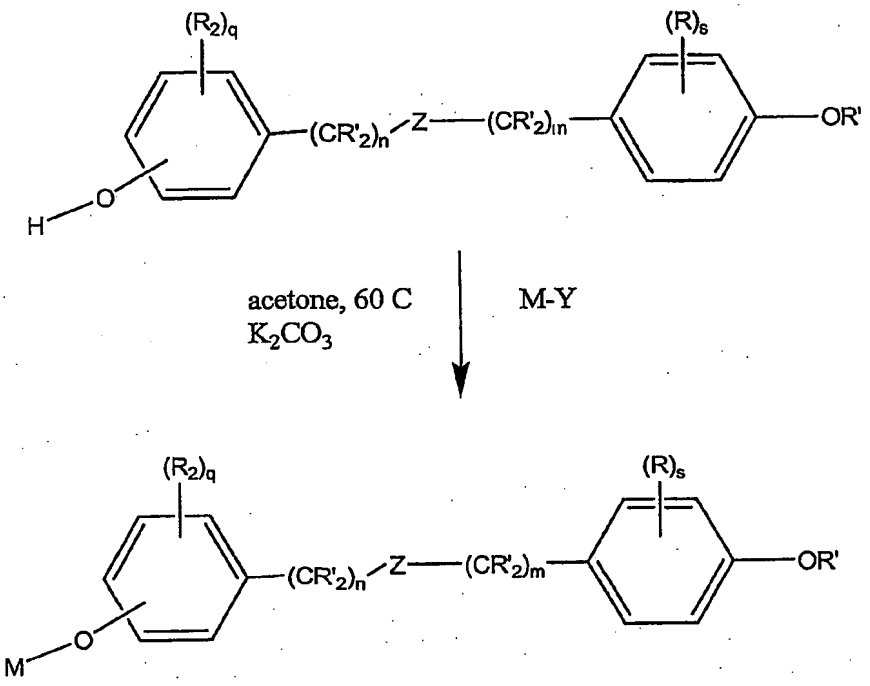
where Y is halogen (Cl, Br, or *I*), B is $-NH_2$, -OH etc., B' is -NH-, -O- etc., which together with =C(O)- forms Z, and the remainder of the variables are as described above.

In various embodiments, the alkylated macromolecular antioxidants of the present invention can be prepared as shown in the following Scheme:



where Y is halogen (Cl, Br, or I), B is -NH_2, -OH etc., B' is -NH-, -O- etc., which together with =C(O)- forms Z, and the remainder of the variables are as described above.

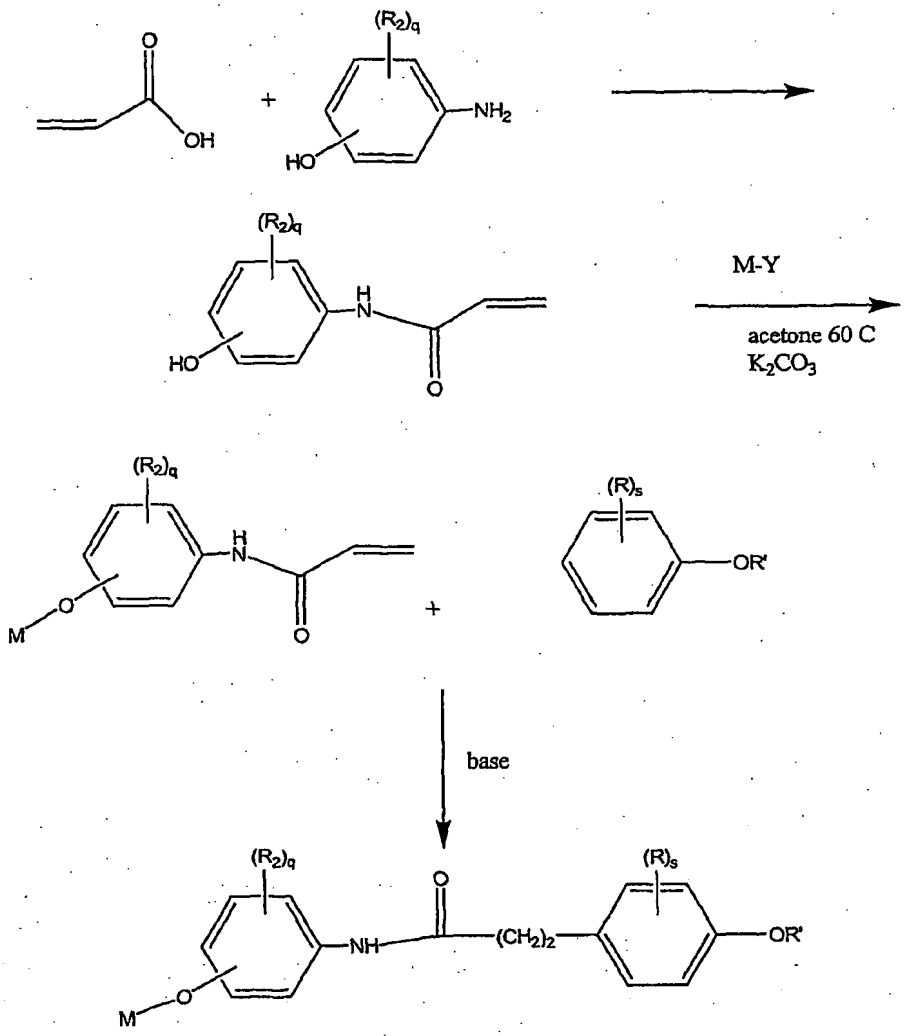
In various embodiments, the alkylated macromolecular antioxidants of the present invention can be prepared as shown in the following Scheme:



where Y is halogen (Cl, Br, or I) and the remainder of the variables are as described above.

hi certain embodiments the compounds are made by, for example, dissolving the phenolic starting material in a suitable solvent, such as, for example, acetone, and adding for example potassium carbonate . In these embodiments the mixture is stirred and a haloalkane for example bromodecane added, over a period of time for example 1 min to 24 hours, 10 minutes to 15 hours, 30 minutes to 2 hours, or 55 minutes to 65 minutes. In these embodiments the mixture is then refluxed and progress of the reaction is monitored by thin layer chromatography. After completion of the reaction, potassium carbonate is filtered and the solvent is removed under vacuum to get the crude solid. The solid is obtained was re-dissolved in hexane and filtered to obtain the pure solid.

hi various embodiments, the alkylated macromolecular antioxidants of the present invention can be prepared as shown in the following Scheme:

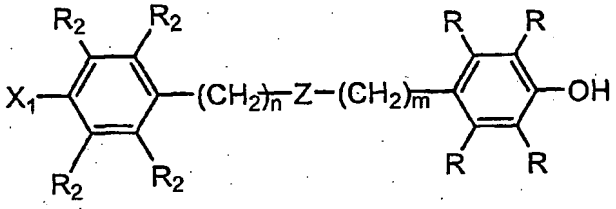


where Y is halogen (Cl, Br, or I) and the remainder of the variables are as described above.

In various embodiments, intermediates in the compounds of the present invention can be prepared by methods described in U.S. Publication No.s: 2006/0041094 and 2006/0041087 U.S. Application No.s: 11/292,813, 11/293,050, 11/293,049 and 11/293,844 the entire teachings of each of these references are incorporated herein by reference. In various embodiments, compounds represented by Structural Formula 3 can be prepared by methods described in U.S. Publication No.s: 2006/0041094 and 2006/0041087 U.S. Application No.s: 11/292,813, 11/293,050, 11/293,049 and 11/293,844 the entire teachings of each of these references are incorporated herein by reference.

The compositions comprising a compound of Structural Formula 1 and a compound of Structural Formula 2 are prepared in certain embodiments by physically mixing the two compounds in certain ratios using a vortex mixture. The compositions comprising a compound of Structural Formula 1 and a compound of Structural Formula 2 are prepared in certain embodiments by dissolving the compounds in an organic solvent, homogenizing it and removing the organic solvent. Suitable organic solvents are any solvents known in the art in which the compounds can be dissolved or suspended. The compounds can be mixed or dissolved under a range of temperatures including from 0 to 100 ^{0}C, from 10 to 50 ^{0}C or from 15 to 30 ^{0}C. The temperature at which the compounds are mixed will vary depending on the starting material, for example, powder starting material can be physically mixed at room temperature, alternatively powder or liquid starting material can be heated to dissolve in suitable solvents.

hi various embodiments, the alkylated macromolecular antioxidants of formula I can be prepared by the modification of the compounds of formula II.



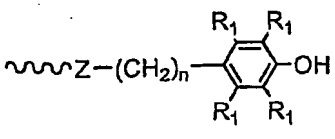
II

wherein, independently for each occurrence,

n and m are integers from 0 to 6, inclusive;

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -CH=N-, -C(O)-, -O-, -S-, -C(O)OC(O)-, or a bond;

R is H, C_{1-6} alkyl, -OH, $-NH_2$, -SH, aryl, ester, or



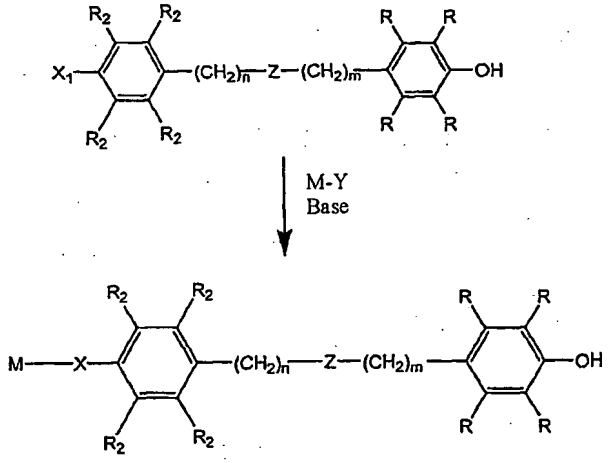
, wherein at least one R adjacent to the -OH group is a bulky alkyl group;

R_1 is H, Ci_{-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or ester wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group; and

R_2 is H, C_{1-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or ester wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group;

X_1 is -C(O)OH, -OH, $-NH_2$, CHO, -SH, or C1-C6 alkyl ester.

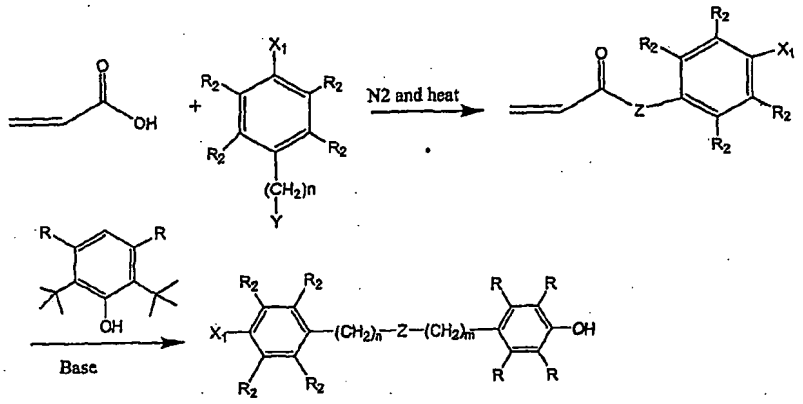
hi various embodiments, the compounds of formula I can be prepared by the modification of compound of formula II as shown in Scheme-2.



Scheme-2

hi various embodiments, the compounds of formula II can be prepared by methods described in U.S. Provisional Application No.: 60/590,575, filed July 23, 2004, Title: Antioxidant Macromonomers and Polymers and methods of making and using the same; U.S. Provisional Application No.: 60/590,646, filed July 23, 2004; Title: Antioxidant Macromonomers and Polymers and methods of making and using the same; Atty. Docket No.: 3805.1000-000, U.S. Provisional Application filed December 3, 2004; Atty. Docket No.: 3805.1002-000, U.S. Provisional Application filed December 3, 2004, Title: ONE POT PROCESS FOR MAKING POLYMERIC ANTIOXIDANTS by Kumar, *et al.* The entire teachings of these references are incorporated herein by reference.

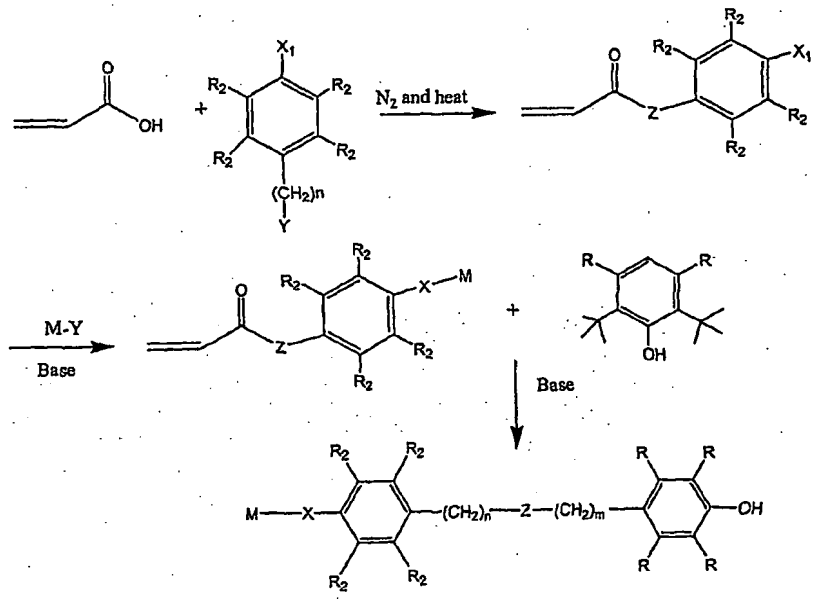
In various embodiments, the compounds of formula II can also be prepared by the method shown in Scheme 1.



II

Scheme-1

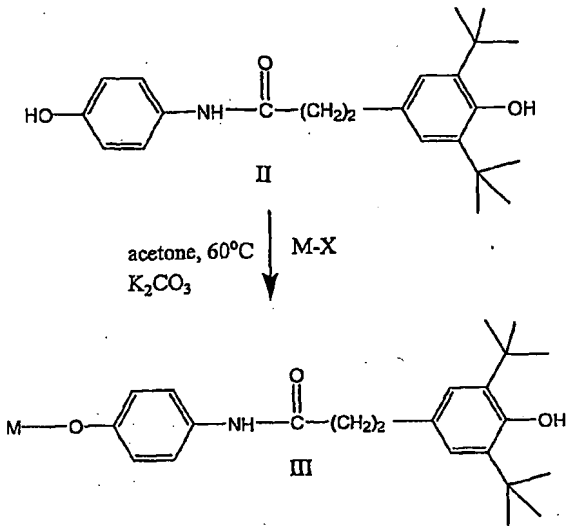
In various embodiments, the compounds of formula II can also be prepared by the method shown in scheme-3



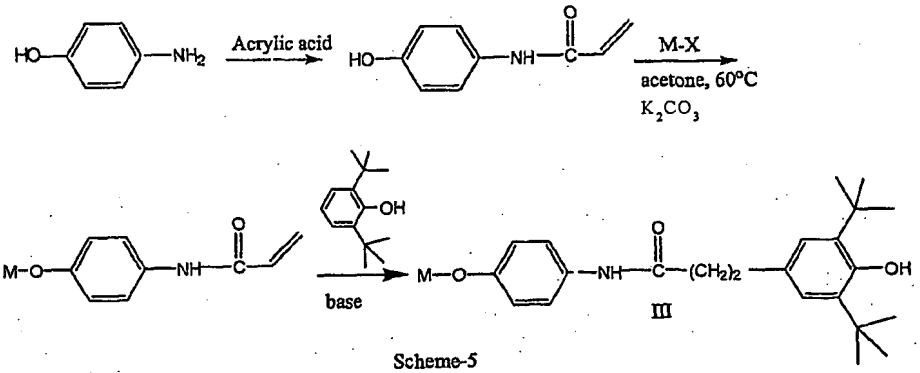
II

Scheme-3

In various embodiments, the compounds of formula III can be prepared by a method shown in scheme 4 or scheme 5:



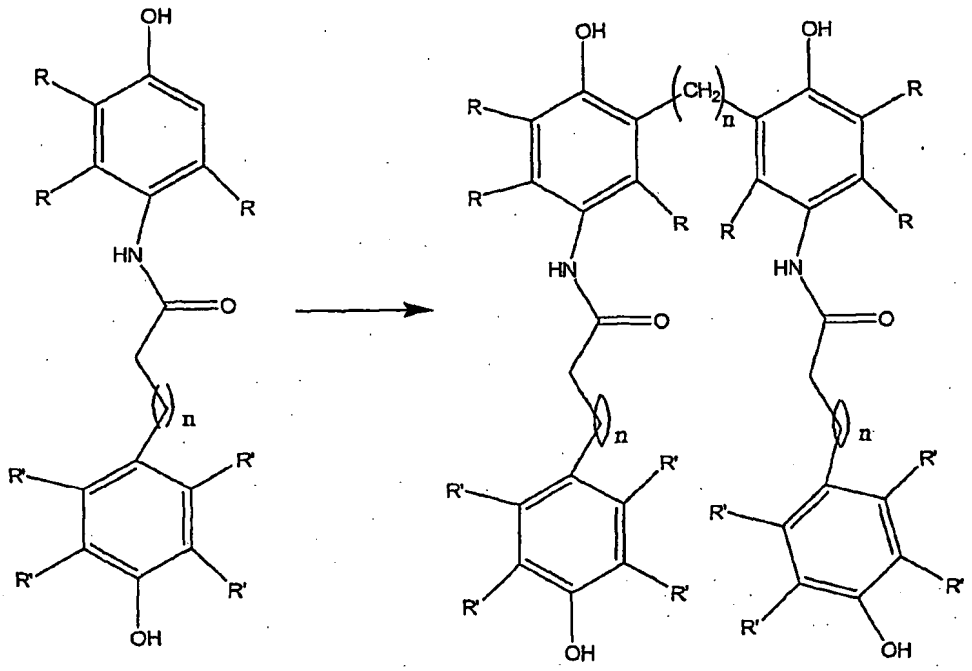
Scheme-4



Scheme-5

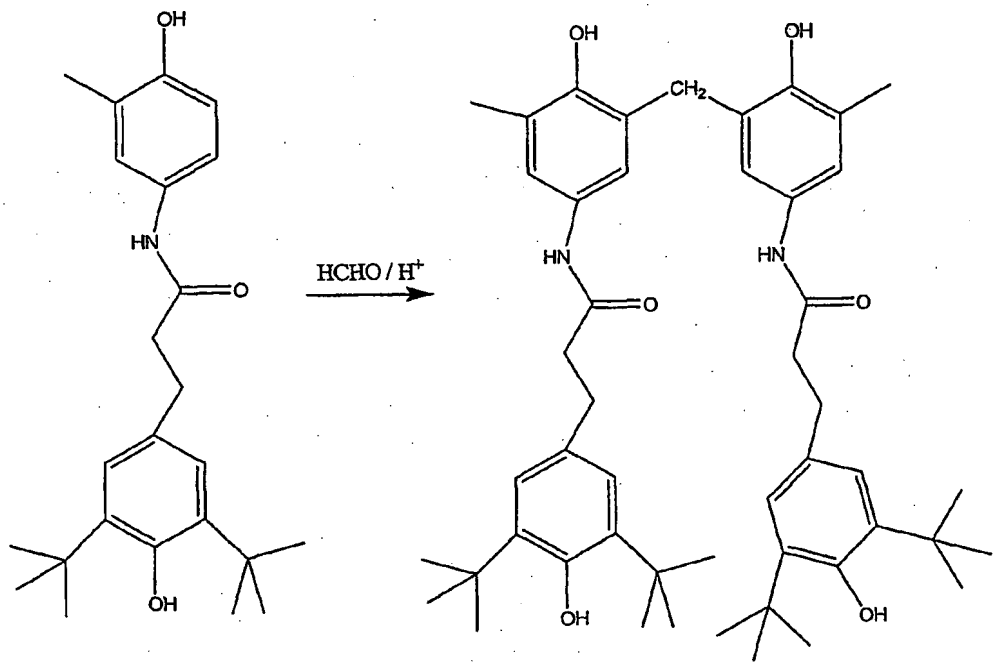
Where M is C1-C20 long linear or branched alkyl chains, and X is a halogen Cl, Br or I.

In various embodiments, the polymers of the present invention can be prepared as shown in the following Scheme:

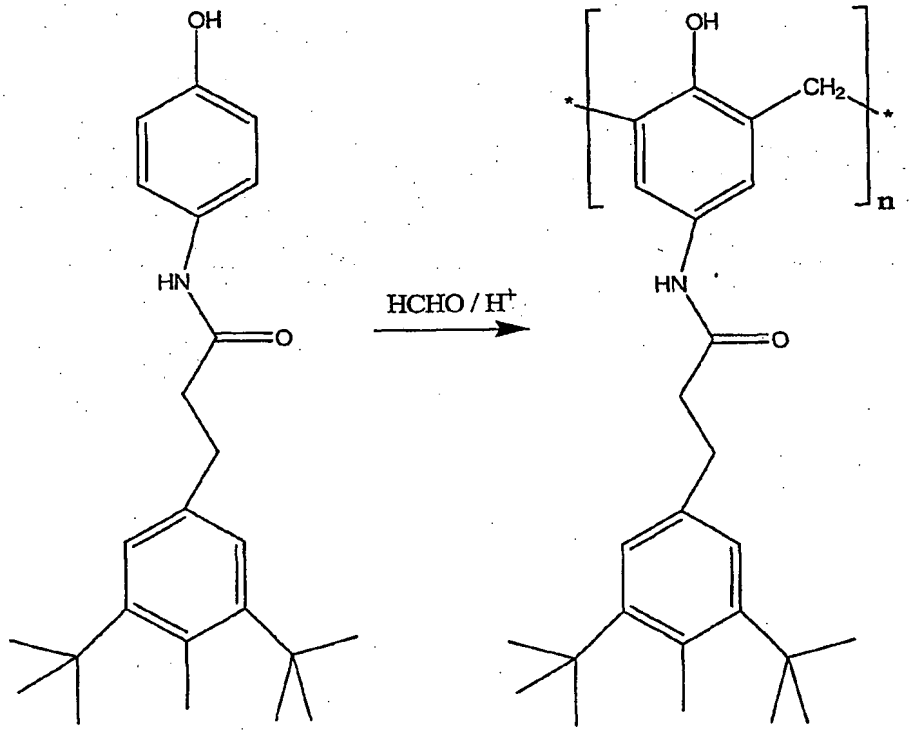


In certain embodiments the present invention is a method of making the polymers of the present invention comprising the steps of dissolving or suspending the starting material in a suitable solvent, such as, methanol or ethanol; adding a suitable reagent, such as, an aldehyde, for example, paraformaldehyde under suitable acidic conditions, such as, for example in the presence of hydrochloric acid. The mixture of the starting material, solvent acid and reagent can then be refluxed at between 0 and 100 ^{0}C, between 10 and 90 ^{0}C, between 20 and 80 ^{0}C, between 40 and 70 ^{0}C or between 60 and 70 ^{0}C. The progress of the reaction can be monitored by thin-layer chromatography. After completion of the reaction the solvent can be removed by distillation under vacuum. The remaining solid can then be washed with water and dried to obtain the polymer.

In various embodiments, the polymers of the present invention can be prepared as shown in the following Scheme:



In various embodiments, the polymers of the present invention can be prepared as shown in the following Scheme:



In certain embodiments these macromolecular antioxidants and polymers can have significantly higher antioxidant activities along with improved thermal stability

and performance in a wide range of materials including but not limited to plastics, elastomers, lubricants, petroleum based products (lubricants, gasoline, aviation fuels, and engine oils), cooking oil, cosmetics, processed food products, compared to commercially available antioxidants. In certain embodiments the present invention also discloses the superior performance of macromolecules of the formula I in materials including but not limited to polyolefms.

The compounds and polymers of the present invention can be used as antioxidants to inhibit oxidation of an oxidizable material. Such as, for example to increase the shelf life of an oxidizable material.

The antioxidant compounds and polymers of the present invention can be employed to inhibit the oxidation of an oxidizable material, for example by contacting the material with an antioxidant compound or polymer of the present invention.

For purposes of the present invention, a method of "inhibiting oxidation" is a method that inhibits the propagation of a free radical-mediated process. Free radicals can be generated by heat, light, ionizing radiation, metal ions and some proteins and enzymes. Inhibiting oxidation also includes inhibiting reactions caused by the presence
of oxygen, ozone or another compound capable of generating these gases or reactive equivalents of these gases.

As used herein the term "oxidizable material" is any material which is subject to oxidation by free-radicals or oxidative reaction caused by the presence of oxygen, ozone or another compound capable of generating these gases or reactive equivalents thereof.

In certain embodiments, the oxidizable material is an organic polymer or plastic. In certain embodiments, the oxidizable material is an elastomer. In certain embodiments, the oxidizable material is a lubr cant. hi certain embodiments, the oxidizable material is a petroleum based product. hi certain embodiments, the oxidizable material is an edible oil or cooking oil. hi certain embodiments, the oxidizable material is a cosmetic. In certain embodiments, the oxidizable material is a processed food product.

In particular the oxidizable material is a lubricant or a mixture of lubricants.

The shelf life of many materials and substances contained within the materials, such as packaging materials, are enhanced by the presence of the antioxidants of the present invention. The addition of an antioxidant of the present invention to a packaging material is believed to provide additional protection to the product contained inside the package. hi addition, the properties of many packaging materials themselves, particularly polymers, are enhanced by the presence of an antioxidant regardless of the application (i.e., not limited to use in packaging). Common examples of packaging materials include paper, cardboard and various plastics and polymers. A packaging material can be coated with an antioxidant (e.g., by spraying the antioxidant or by applying as a thin film coating), blended with or mixed with an antioxidant, or otherwise have an antioxidant present within it. hi one example, a thermoplastic such as polyethylene, polypropylene or polystyrene can be melted in the presence of an antioxidant in order to minimize its degradation during the polymer processing.

The lifetime of lubricants, lubricant oils, mixtures thereof and compositions comprising lubricants and lubricant oils in general can be improved by contacting the lubricant, lubricant oil, mixtures thereof or composition comprising the lubricant or lubricant oil or mixtures thereof with compounds of the present invention, as described herein.

In certain embodiments of the present invention, polyolefins and mixtures of polyolefins can be stabilized by contacting the polyolefin or mixture of polyolefins with a compound or polymer of the present invention. These polyolefins and mixtures of polyolefins, include, but are not limited to substituted polyolefins, polyacrylates, polymethacrylates and copolymers of polyolefins. The following are examples of some types of polyolefins which can be stabilized by the methods of the present invention:

1. Polymers of monoolefins and diolefms, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-l-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-

UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE) and ultra low density polyethylene (ULDPE).

Polyolefms, i.e. the polymers of monoolefms exemplified in the preceding paragraph, for example polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

i) radical polymerization (normally under high pressure and at elevated temperature).

ii) catalytic polymerization using a catalyst that normally contains one or more than one metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either p- or s-coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(IH) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerization medium. The catalysts can be used by themselves in the polymerization or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, Ha and/or Ilia of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

2. Mixtures of the polymers mentioned under 1., for example, mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

3. Copolymers of monoolefms and diolefms with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene

copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

4. Blends of polymers mentioned under 1. with impact modifiers such as ethylene-propylene-diene monomer copolymers (EPDM), copolymers of ethylene with higher alpha-olefins (such as ethylene-octene copolymers), polybutadiene, polyisoprene, styrene-butadiene copolymers, hydrogenated styrene-butadiene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers. These blends are commonly referred to in the industry as TPO's (thermoplastic polyolefins).

In certain particular embodiments polyolefins of the present invention are for example polypropylene homo- and copolymers and polyethylene homo- and copolymers. For instance, polypropylene, high density polyethylene $(HDPE)_5$ linear low density polyethylene (LLDPE) and polypropylene random and impact (heterophasic) copolymers.

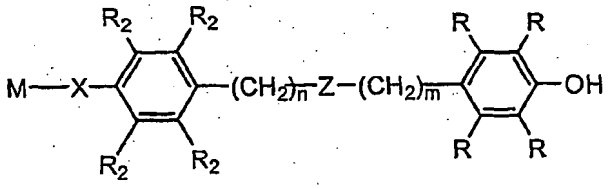
In certain embodiments of the present invention, 50% to 20% by weight of the antioxidants of the present invention are added to the polyolefin. In certain other embodiments of the present invention, 10% to 5% by weight of the antioxidants of the present invention are added to the polyolefin. In certain other embodiments of the present invention, 0.1% to 2% by weight of the antioxidants of the present invention are added to the polyolefin. In certain other embodiments of the present invention, 0.001% to 0.5% by weight of the antioxidants of the present invention are added to the polyolefin. This percentage varies depending upon their end application and type of the polyolefin.

In certain embodiments of the present invention the antioxidants of the present invention are usually added to the polyolefin with stirring at between 0 and 100 °C, between 10 and 80 °C, between 20-30°C or at room temperature.

In certain embodiments the antioxidants of the present invention can be mixed with other antioxidants or additives to produce formulations, such as those described in Docket No.: 3805.1009-000; Provisional Patent Application No. 60/742,150, filed December 2, 2005, Title: Lubricant Composition, by Kumar, Rajesh, et al., and Docket No.: 3805.1010-000; Provisional Patent Application No. 60/731,325, filed October 27, 2005, Title: Stabilized Polyolefin Composition, by Kumar, Rajesh, et al., the entire contents of each of which are incorporated herein by reference.

Without wishing to be bound be theory it is believed that alkylation at the phenolic oxygen or ortho to the phenolic hydroxy (or alkoxy) group increases secondary properties of the antioxidants such as maintaining the melt flow index (MFI), decreasing the yellowing index (YT).

In certain embodiments the present invention relates to a method of preventing oxidation comprising combining an oxidizable material with a compound represented by Structural Formula I:

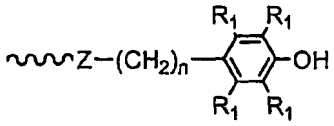


I

wherein, independently for each occurrence,

n and m are integers from 0 to *6*, inclusive;

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -CH=N-, -C(O)-, -O-, -S-, -C(O)OC(O)-, or a bond;



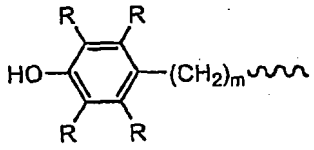
Ris H, C_{1-6} alkyl, -OH, $-NH_2$, -SH, aryl, ester, or ,

wherein at least one R adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, *tert-butyl*, 2-propyl, 1,1-dimethylhexyl, and the like);

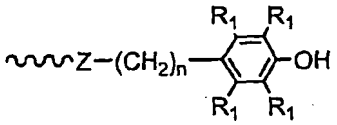
Ri is H, C_{1-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or C1-C6 alkyl ester wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, sec-butyl, tert-butyl, 2-propyl, 1,1-dimethylhexyl, and the like); and

R_2 is H, C_{1-6} alkyl, aryl, aralkyl, -OH, $-NH_2$, -SH, or ester, wherein at least one R_1 adjacent to the -OH group is a bulky alkyl group (e.g., butyl, .sec-butyl, *tert*-butyl, 2-propyl, 1,1-dimethylhexyl, and the like);

X is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -CH=N-, -C(O)-, -O-, -S-, -C(O)OC(O)-, or a bond;

M is H, aryl, C-I to C-20 linear or branched alkyl chain with or without any functional group anywhere in the chain, or  , wherein m and each R is independently as described above;

wherein

R_2 is H, C_{1-6} alkyl, -OH, $-NH_2$, -SH, aryl, ester, or  , wherein at least one R_2 is -OH and n, Z, and each R1 are independently as described above.

In certain embodiments, the oxidizable material is an organic polymer or plastic. In certain embodiments, the oxidizable material is an elastomer. In certain embodiments, the oxidizable material is a lubricant. In certain embodiments, the oxidizable material is a petroleum based product. In certain embodiments, the oxidizable material is an edible oil or cooking oil. In certain embodiments, the oxidizable material is a cosmetic. In certain embodiments, the oxidizable material is a processed food product.

EXEMPLIFICATION

Example 1, Improved oxidation induction times of the antioxidants of the present invention in Plastics

The synthesized alkylated macromolecular antioxidants of formula I and in particular of formula III were evaluated and found to have desirable antioxidant properties in plasties. The antioxidant properties of these novel compounds were studied by mixing 5000 ppm of these novel antioxidants in polypropylene and extruding the mixture with a single screw extruder. The oxidative induction time (OIT) values were determined using ASTM D3895 method by differential scanning calorimetry (DSC). The value of OITs in minutes obtained is listed in Table 1.

Table 1. Comparison of performance and properties of various antioxidants of the present invention (AO's)

Compound III M	M.P (°C)	Hexane solubility	OIT @ 5000 ppm in PP (mins)
M= $C_{10}H_{21}$	100-105	5.7 mg/ml	63-75
M=CH_3	170-175	1.2 mg/ml	52
M =C_4H_9	135-140	2 mg/ml	30

FIG 1 is a graph showing superior performance of alkylated macromolecules of Formula III with M = $C_{10}H_{21}$, compared with commercially available antioxidants.

FIG 2 is a high resolution nuclear magnetic resonance (NMR) spectrum of the compound of Formula III having M=$C_{10}H_{21}$.

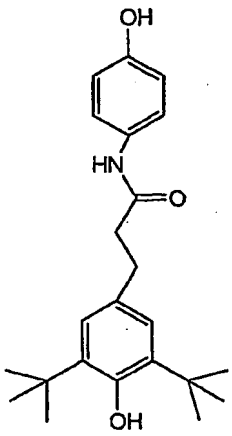
FIG 3 is a Fourier Transform Infrared (FT-IR) spectrum of the compound of Formula III having M=$C_{10}H_{21}$. The assignments of the peaks in Figure 3 are consistent with the structure of the compound.

This data suggests that proposed antioxidants in this disclosure have nearly 2.8 times better when compared with commercially available antioxidant Irganox

1010, and 1.8 times better when compared with commercially available antioxidant Irganox 1330. In this comparison test, each sample was prepared by combining 5000 ppm of antioxidant in polypropylene and extruding using a single screw extruder.

Example 2, Improved secondary properties of the polymeric antioxidants of the present invention in Plastics

The macromolecular antioxidants i and ii:



1

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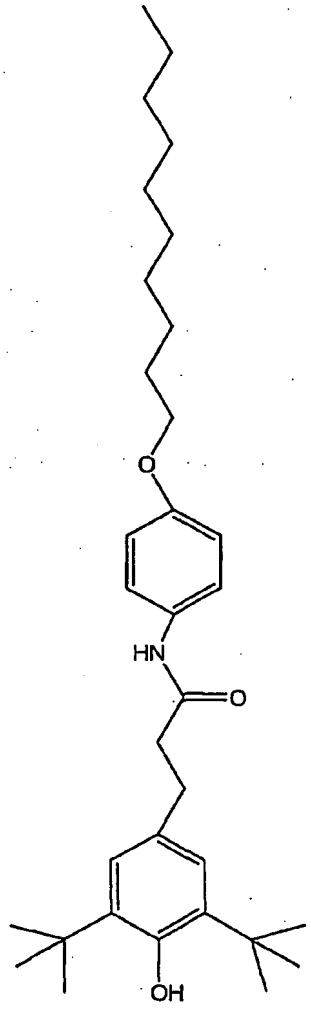
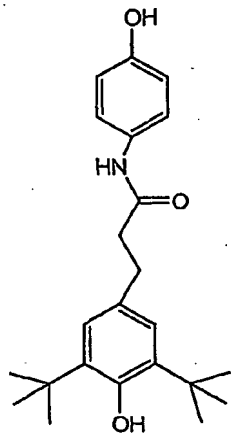


2

i



ii

were evaluated for the antioxidant activity in polypropylene homopolymer (PP) (nominal MFI 4 dg/min) and found to have desirable secondary antioxidant properties. The macromolecular antioxidant i is a composition comprising a 1:2 mixture of the two compounds depicted above. The macromolecular antioxidants i (1000 ppm), ii (1000 ppm) and commercially available Irganox® 1010 (1000 ppm) were formulated with secondary antioxidants (selected from Irgafos® 168 and Irgafos® 126 (1000 ppm)) and acid neutralizer calcium sterate (1000 ppm). The formulations were dry blended in the PP and extruded with a single screw extruder at zone temperatures of 200, 230, 250, 250 °C. The melt flow index (MFI) was measured using ASTM D 1238, the yellowing index (YI) was measured on extruded granules packed in a quartz cuvette.

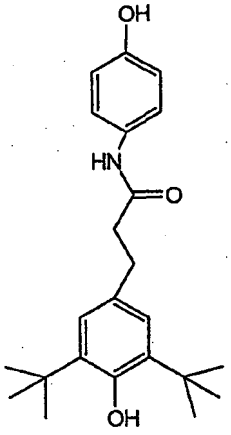
The MFI results are shown in FIG 4 and FIG 5, which demonstrate that the maintenance of melt flow index over five extruder passes for the antioxidant i matches and is slightly superior to commercially available Irganox® 1010 and to the antioxidant ü. These figures also show that substituting Irgafos® 126 for Irgafos® 168 improves the ability of the antioxidant i to maintain the MFI. In FIG 4 and 5 all formulations contain 1000 ppm AO (antioxidant), 1000 ppm Irgafos 168 (except where noted) and 1000 ppm calcium stearate.

The YI results are shown in FIG 6 and FIG 7, which demonstrate that the YI is much improved for antioxidant i over antioxidant ii and also substituting Irgafos®

126 for Irgafos® 168 improves the secondary antioxidant properties of antioxidant i. In FIG 6 and 7 all formulations contain 1000 ppm AO, 1000 ppm Irgafos 168 (except where noted) and 1000 ppm calcium stearate.

Example 3, Improved oxidation induction times of the polymeric antioxidants of the present invention in Plastics

The macromolecular antioxidants i and ii:



1

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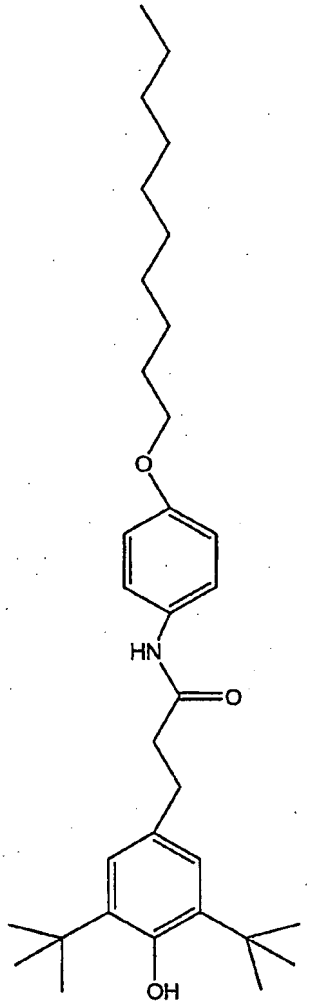
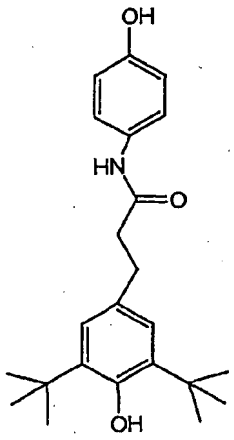


2

i



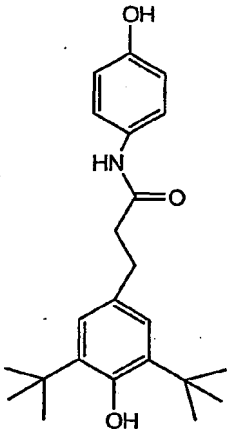
ii

were evaluated for the antioxidant activity in polypropylene homopolymer (PP) (nominal MFI 4 dg/min) and found to have desirable secondary antioxidant properties. The antioxidants macromolecular antioxidants i (1000 ppm), ii (1000 ppm) and commercially available Irganox® 1010 (1000 ppm) were formulated with secondary antioxidants (selected from Irgafos® 168 and Irgafos® 126 (1000 ppm)) and acid neutralizer calcium sterate (1000 ppm). The formulations were dry blended in the PP and extruded with a single screw extruder at zone temperatures of 200, 230, 250, 250 ^{0}C. The oxidative induction time (OIT) values were determined using ASTM D3895 method by differential scanning calorimetry (DSC).

The OIT results are shown in FIG 8, which demonstrates that the oxidative induction times for antioxidant i is far superior to commercially available Irganox® 1010. Even after five extruder passes PP samples mixed with antioxidant i show higher OIT values that PP samples mixed with Irganox® 1010 after one extruder pass. All formulations in FIG 8 contain 1000 ppm AO, 1000 ppm Irgafos® 168 and 1000 ppm calcium stearate.

Example 4, Heat aging of the polymeric antioxidants of the present invention in Plastics

The macromolecular antioxidants i and ii:



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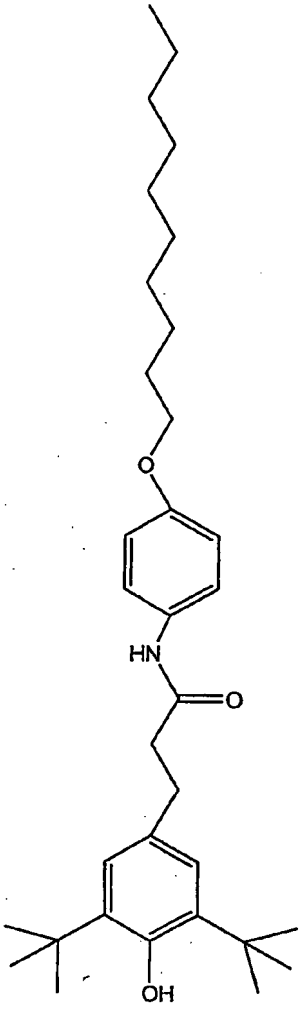
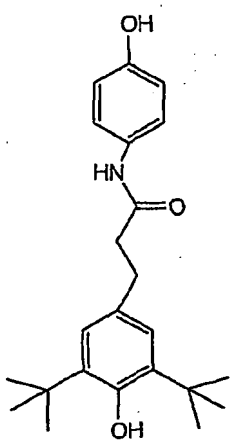


1 : 2

i

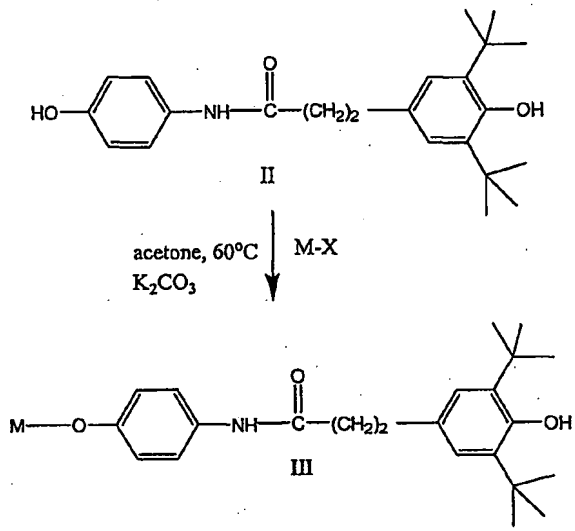


ii

were evaluated for the antioxidant activity in polypropylene homopolymer (PP) (nominal MFI 4 dg/min) and found to have desirable secondary antioxidant properties. The antioxidants macromolecular antioxidants i (1000 ppm), ii (1000 ppm), commercially available Irganox® 1010 (1000 ppm), Irganox® 1330 (1000 ppm) and Irganox® 1076 (1000 ppm) were formulated with secondary antioxidants (Irgafos® 168 (1000 ppm)) and acid neutralizer (calcium sterate (1000 ppm)). The formulations were dry blended in the PP and extruded with a single screw extruder at zone temperatures of 200, 230, 250, 250 ^{0}C. The heat aging was measured by placing a 1.6 mm film of the PP formulations in an oven at 150 ^{0}C and checking the films daily. The films were considered to have failed when cracks appeared on the films when they were subjected to a force, such as, bending.

The heat aging results are shown in FIG 9, which demonstrate that the antioxidant i is superior to antioxidant ii and to commercially available Irganox® 1330 and Irganox® 1076 and is above the typical industry standard of 8 - 9 days. All formulations in FIG 9 are in the form of a substrate extruded firm of 1.6 mm thick. AU formulations contain 1000 ppm AO, 1000 ppm calcium stearate and 1000 ppm Irgafos 168.

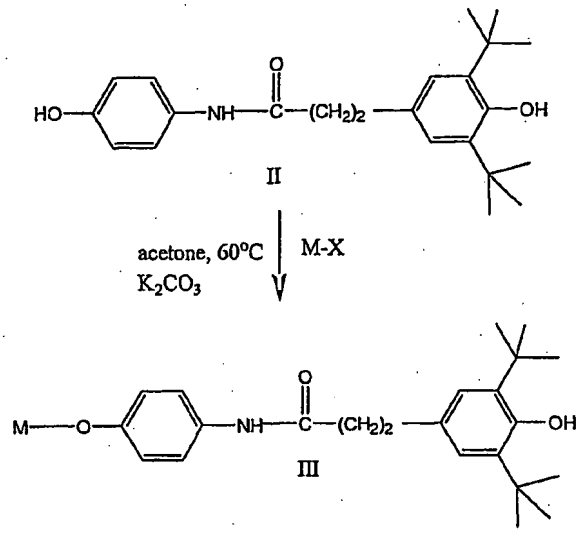
Example 5, synthesis of compounds of the present invention represented by formula III where M is $C_{10}H_{21}$.



Scheme-4

369 g of phenolic starting material above was dissolved in 1.5 L of anhydrous acetone and to that added 136 g of fused potassium carbonate. The reaction mixture was stirred for some time and to that added 220 g of bromodecane over a period of 60 minutes. The reaction mixture was refluxed and progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, potassium carbonate was filtered and the solvent was removed under vacuum to get the crude solid. The solid was obtained was re-dissolved in hexane and filtered to obtain the pure solid.

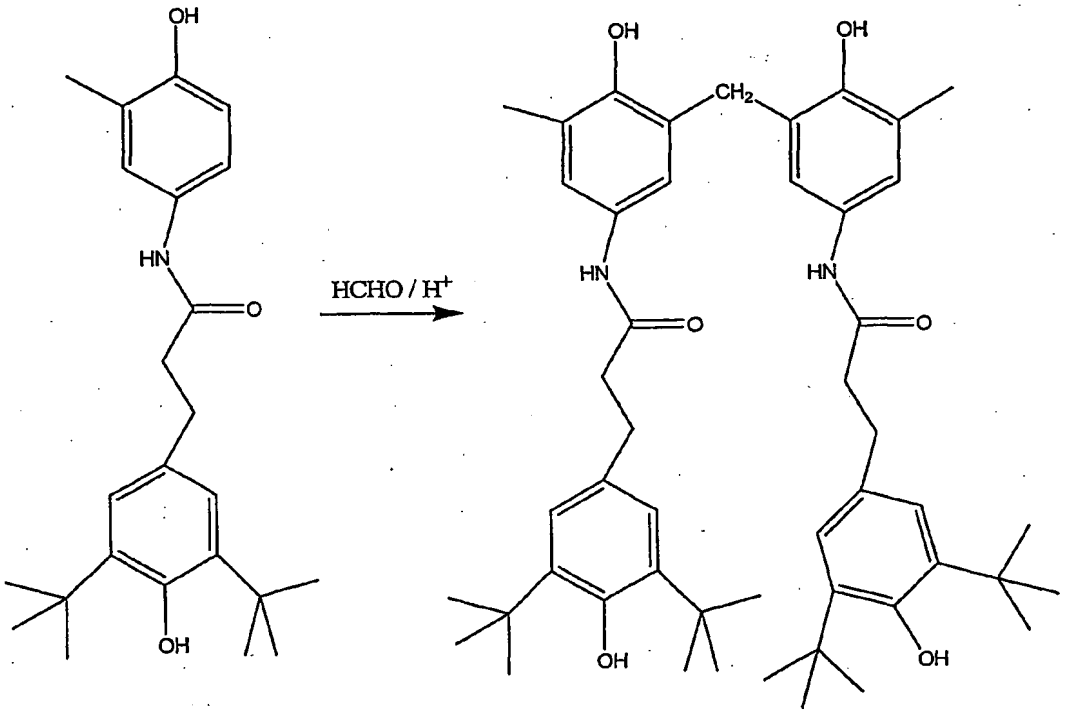
Example 6, synthesis of compounds of the present invention represented by formula IH where M is C_1H_3.



Scheme-4

75 g of phenolic compound represented II was dissolved in 200 ml of anhydrous acetone and to that added 25 g of fused potassium carbonate. The resultant reaction mixture was stirred for 10 minutes followed by the addition of 30 g of methyl iodide and refluxed for a predetermined time period. The product methylated II was isolated by filtration of potassium carbonate and drying the filtrate by removing the solvent under vacuum.

Example 7, synthesis of polymers of the present invention:



1.5g of 3, 5-bis (l,l-dimethylethyl)-4-hydroxy-N-(4-hydroxy-3-Methyl phenyl)-benzenepropanamide, and paraformaldehyde were dissolved in 20 ml of methanol. To that added 0.1 ml of hydrochloric acid and the reaction mixture was refluxed at 65^{0}C. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the solvent was removed by distillation under vacuum. The solid obtained after distillation of the solvent was washed with water and dried to obtain the resultant product.

The entire contents of each of the following are incorporated herein by reference.

Docket No.: 3805.1000-000; Provisional Patent Application No.: 60/632,893, filed December 3, 2004, Title: Process For The Synthesis Of Polyalkylphenol Antioxidants, by Suizhou Yang, et al;

Docket No.: 3805.1000-003; Patent Application Serial No.: 11/292,813 filed December 2, 2005, Title: Process For The Synthesis Of Polyalkylphenol Antioxidants, by Suizhou Yang, et al;

DocketNo.: 3805.1001-000; Provisional Patent Application No.: 60/633,197, filed December 3, 2004, Title: Synthesis Of Sterically Hindered Phenol Based Macromolecular Antioxidants, by Ashish Dhawan, et al.;

Docket No.: 3805.1001- 003; Patent Application Serial No.: 11/293,050; filed December 2, 2005, Title: Synthesis Of Sterically Hindered Phenol Based Macromolecular Antioxidants, by Ashish Dhawan, et al.;

Docket No.: 3805.1002-000; Provisional Patent Application No.: 60/633,252, filed December 3, 2004, Title: One Pot Process For Making Polymeric Antioxidants, by Vijayendra Kumar, et al.;

Docket No.: 3805.1002-003; Patent Application Serial No.: 11/293,049; filed December 2, 2005, Title: One Pot Process For Making Polymeric Antioxidants, by Vijayendra Kumar, et al.;

Docket No.: 3805.1003-000; Provisional Patent Application No.: 60/633,196, filed December 3, 2004, Title: Synthesis Of Aniline And Phenol-Based Macromonomers And Corresponding Polymers, by Rajesh Kumar, et al.;

Docket No.: 3805.1003-003; Patent Application Serial No.: 11/293,844; filed December 2, 2005, Title: Synthesis Of Aniline And Phenol-Based Macromonomers And Corresponding Polymers, by Rajesh Kumar, et al.;

Docket No.: 3805.1004-002; Patent Application No.: 11/184,724, filed July 19, 2005, Title: Anti-Oxidant Macromonomers And Polymers And Methods Of Making And Using The Same, by Ashok L. Cholli;

Docket No.: 3805.1004-005; Patent Application No. 11/184,716, filed July 19, 2005, Title: Anti-Oxidant Macromonomers And Polymers And Methods Of Making And Using The Same, by Ashok L. Cholli;

Docket No.: 3805.1005-000; Patent Application No.: 11/360,020, filed February 22, 2006, Title: Nitrogen And Hindered Phenol Containing Dual Functional Macromolecules: Synthesis And Their Antioxidant Performances In Organic Materials, by Rajesh Kumar, et al.

DocketNo.: 3805.1006-000; Provisional Patent Application No.: 60/655,169, filed March 25, 2005, Title: Alkylated Macromolecular Antioxidants And Methods Of Making, And Using The Same, by Rajesh Kumar, et al.

Docket No.: 3805.1007-000; Provisional Patent Application No. 60/731,125, filed October 27, 2005, Title: Macromolecular Antioxidants And Polymeric Macromolecular Antioxidants, by Ashok L. Cholli, et al.

Docket No.: 3805.1008-000; Provisional Patent Application No. 60/731,021, filed October 27, 2005, Title: Macromolecular Antioxidants Based On Sterically Hindered Phenols And Phosphites, by Ashok L. Cholli, et al.

Docket No.: 3805.1009-000; Provisional Patent Application No. 60/742,150, filed December 2, 2005, Title: Lubricant Composition, by Kumar, Rajesh, et al.

Docket No.: 3805.1010-000; Provisional Patent Application No. 60/731,325, filed October 27, 2005, Title: Stabilized Polyolefm Composition, by Kumar, Rajesh, et al.

Docket No.: 0813.2006-003; Patent Application No.: 11/040,193, filed January 21 2005, Title: Post-Coupling Synthetic Approach For Polymeric Antioxidants, by Ashok L. Choll, et al.;

Docket No.: 0813.2006-002; Patent Application No.: PCT/US2005/001948, filed January 21, 2005, Title: Post-Coupling Synthetic Approach For Polymeric Antioxidants, by Ashok L. Cholli et al.;

Docket No.: 0813.2002-008; Patent Application No.: PCT/US2005/001946, filed January 21 2005, Title: Polymeric Antioxidants, by Ashok L. Choll, et al.;

Docket No.: 0813.2002-006; Patent Application No.: PCT/US03/10782, filed April 4, 2003, Title: Polymeric Antioxidants, by Ashok L. Choll, et al.;

Docket No.: 0813.2002-004; Patent Application No.: 10/761,933, filed January 21, 2004, Title: Polymeric Antioxidants, by Ashish Dhawan, et al.;

Docket No.: 0813.2002-001; Patent Application No.: 10/408,679, filed April 4, 2003, Title: Polymeric Antioxidants, by Ashok L. Choll, et al.;

US patent No.: US 6,770,785 B1

US patent No.: US 5,834,544

Neftekhimiya (1981), 21(2): 287-298.

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention.

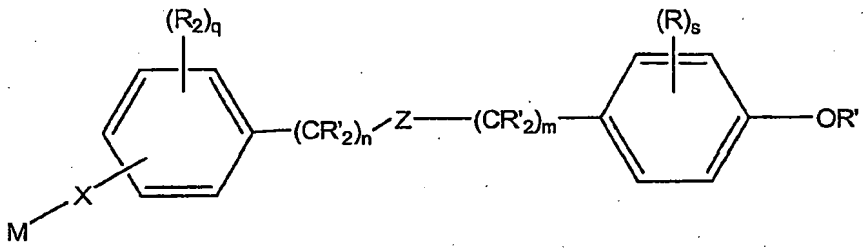
EQUIVALENTS

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.

CLAIMS

What is claimed is:

1. A compound represented by the following Structural Formula:

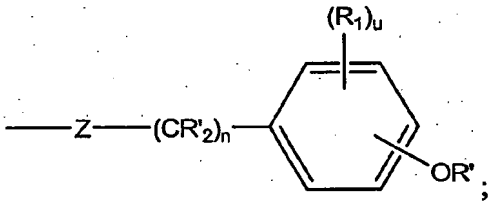


wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond;

each R' is independently -H or optionally substituted alkyl;

each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted

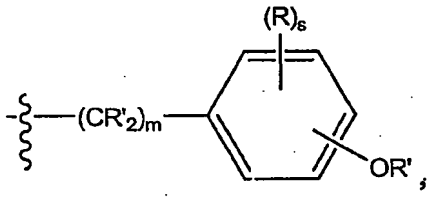


ester, -OH, $-NH_2$, -SH, or ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

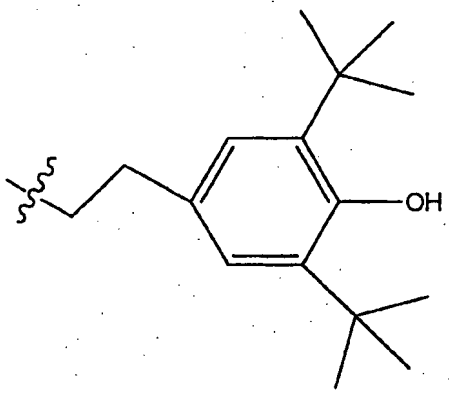
each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

M is an alkyl or 

each n and m are independently integers from 0 to 6; and

each s, q and u are independently integers from 0 to 4;



wherein M is not when X is -C(O)O- or-OC(O) -.

2. The compound of Claim 1, wherein:

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-;

R' is -H;

each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl;

each R_2 is independently an optionally substituted alkyl;

X is -0-;

M is an alkyl;

each n and m are independently integers from Oto 2; and

each s and q are independently integers from Oto 2.

3. The compound of Claim 2, wherein:

Z is -C(O)NH- or -NHC(O)-;

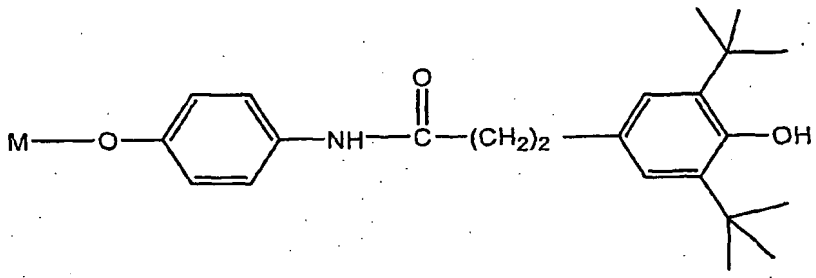
each R is independently an alkyl or an alkoxycarbonyl;

each R_2 is independently an alkyl; and

s is 2.

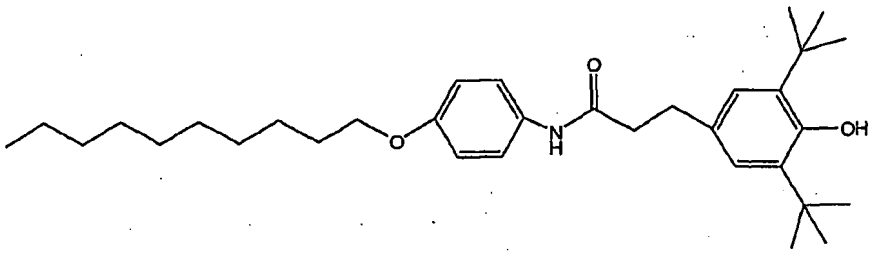
4. The compound of Claim 3, wherein each R is independently an alkyl group.

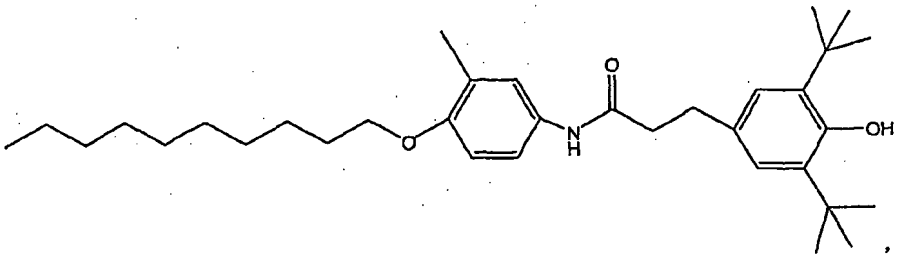
5. The compound of Claim 4, wherein the compound is represented by the following Structural Formula:

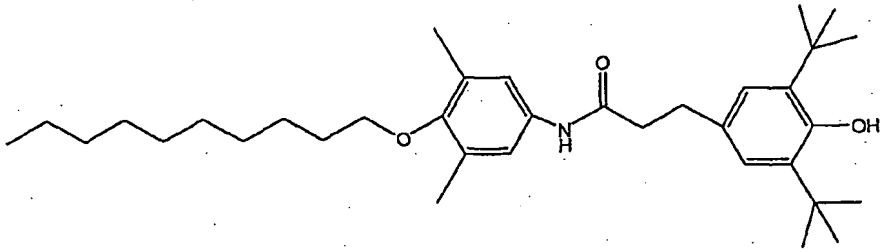


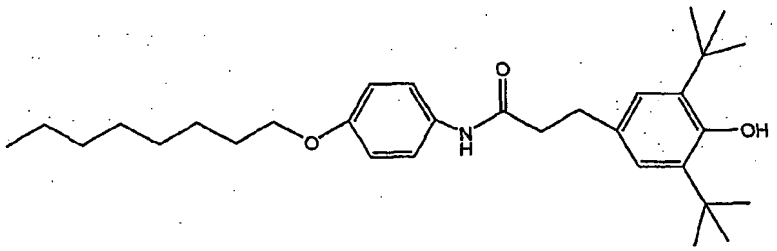
wherein M is a C1 to C20 linear or branched alkyl chain.

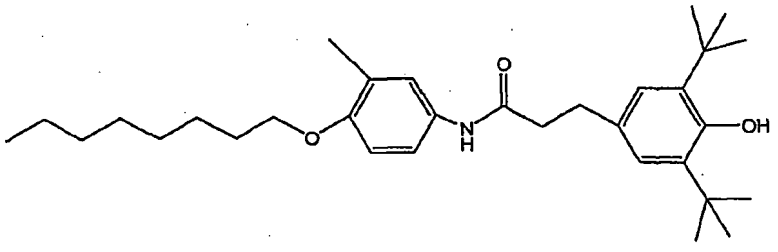
6. The compound of Claim 4, wherein the compound is represented by a Structural Formula selected from:

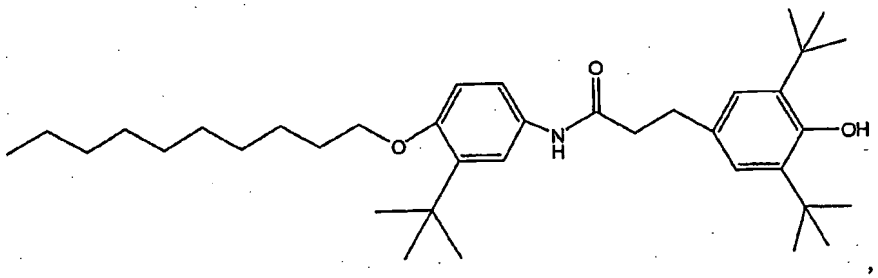


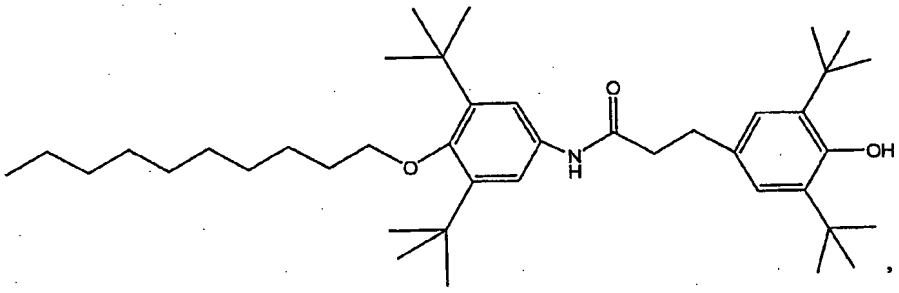


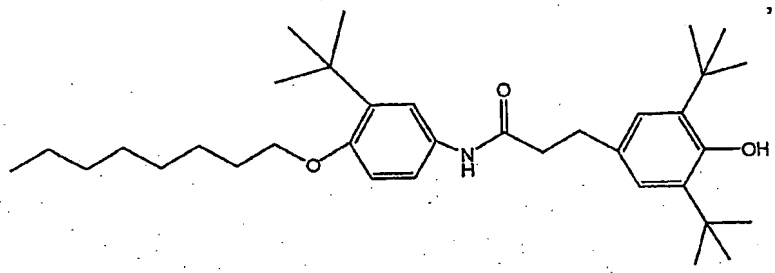


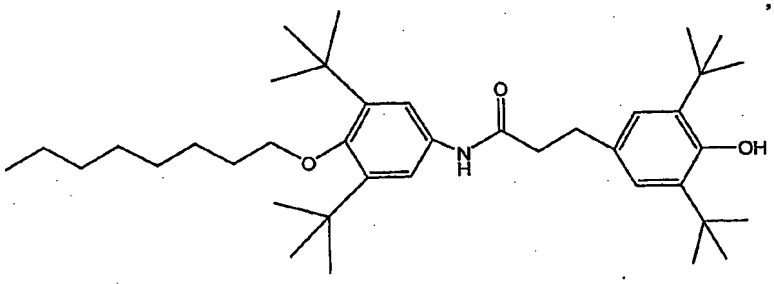


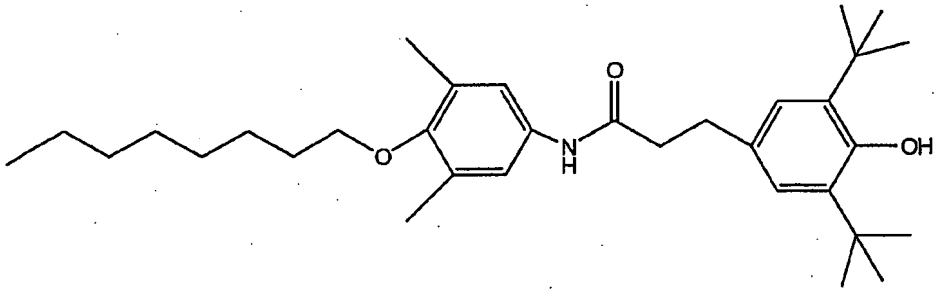












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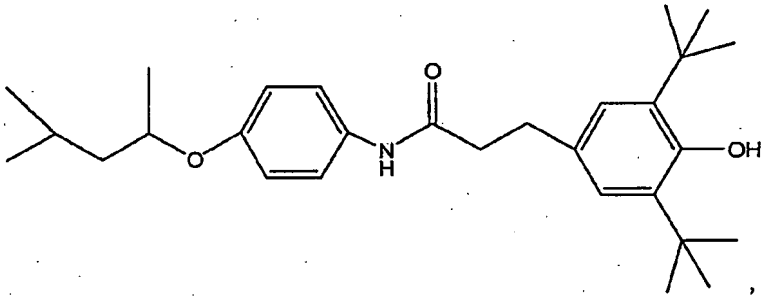
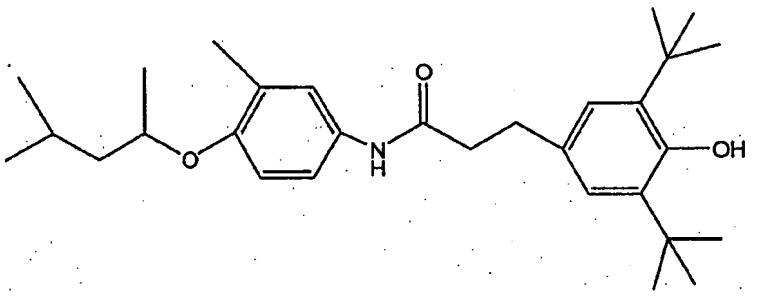
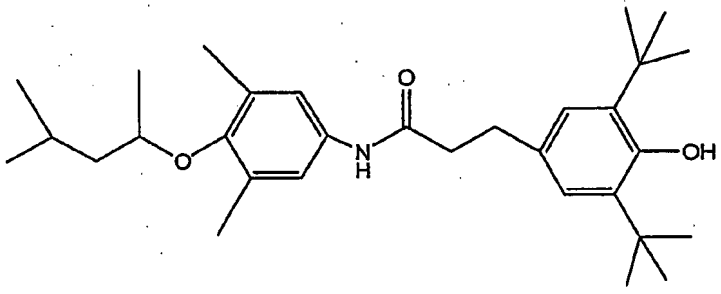


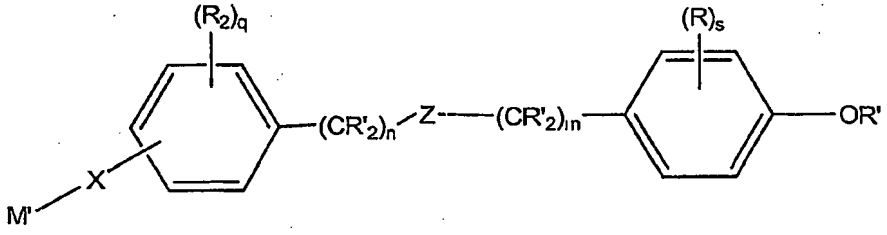
,



or



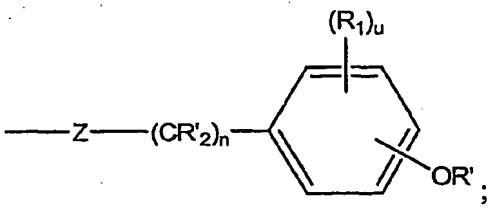
7. A polymer represented by the following Structural Formula:



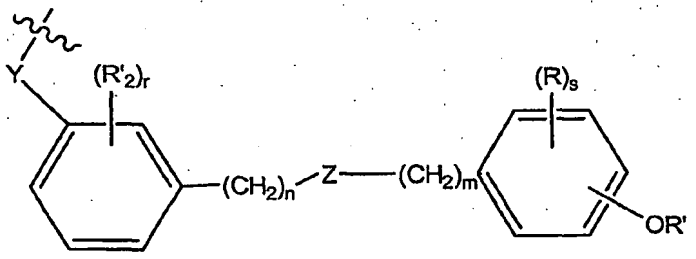
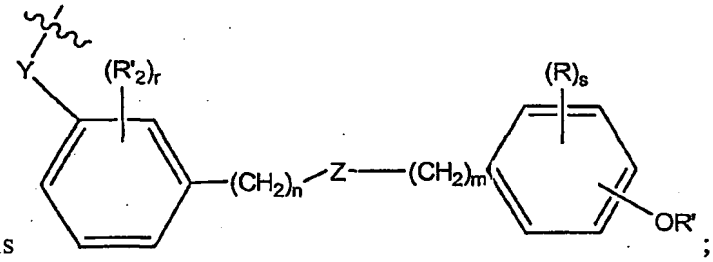
wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -O-, -S-, -C(O)OC(O)- or a bond;

each R' is independently -H or optionally substituted alkyl;

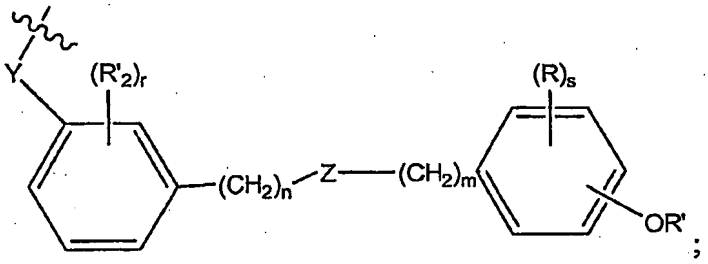
each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH, or  ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH or  wherein at least one R_2 is  ;

each R'_2 is independently -M'-X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally

substituted ester, -OH, $-NH_2$, -SH or



X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

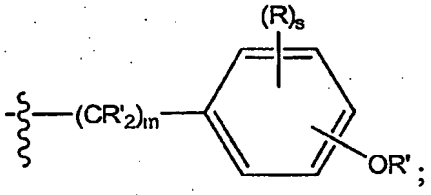
each Y is independently Q-W-Q';

each Q is independently an optionally substituted C1-C20 alkylene group;

each Q' is independently a bond or an optionally substituted C1-C20 alkylene group;

each W is independently arylene, -0-, -S-, -NR'-, -N(OR')-, -C(=N(0R'))-, -C(O)NR'-, -NR'C(O)-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -C(O)OC(O)-, or a bond;

each M' is independently -H, alkyl, or



each n and m are independently integers from Oto 6;

each s, q and u are independently integers from Oto 4; and

r is an integer from Oto 4.

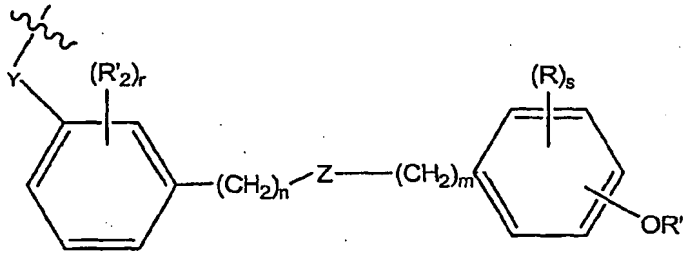
8. The polymer of Claim 7, wherein:

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-;

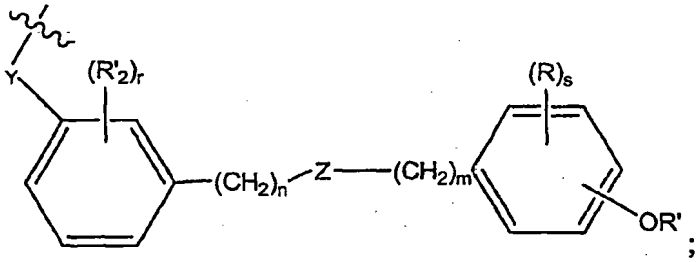
R' is -H;

each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl;

each R_2 is independently an optionally substituted alkyl or



wherein one R_2 is:



;

each R'_2 is independently -M'-X or an optionally substituted alkyl;

each M' is independently - H or alkyl;

X is -O-;

each Q is independently an optionally substituted Cl-ClO alkylene group;

each Q' is independently a bond or an optionally substituted Cl-ClO alkylene group;

each W is independently arylene, -O-, -S-, -NH-, -N(OH)-, -C(=N(OH))-, or abond;

each n and m are independently integers from 0 to 2;

each s and r are independently integers from 0 to 2; and

q is an integer from 1 to 3.

9. The polymer of Claim 8, wherein:

Z is -C(O)NH- or -NHC(O)-;

each R is independently an alkyl or an alkoxycarbonyl; and

s is 2.

10. The polymer of Claim 9, wherein:

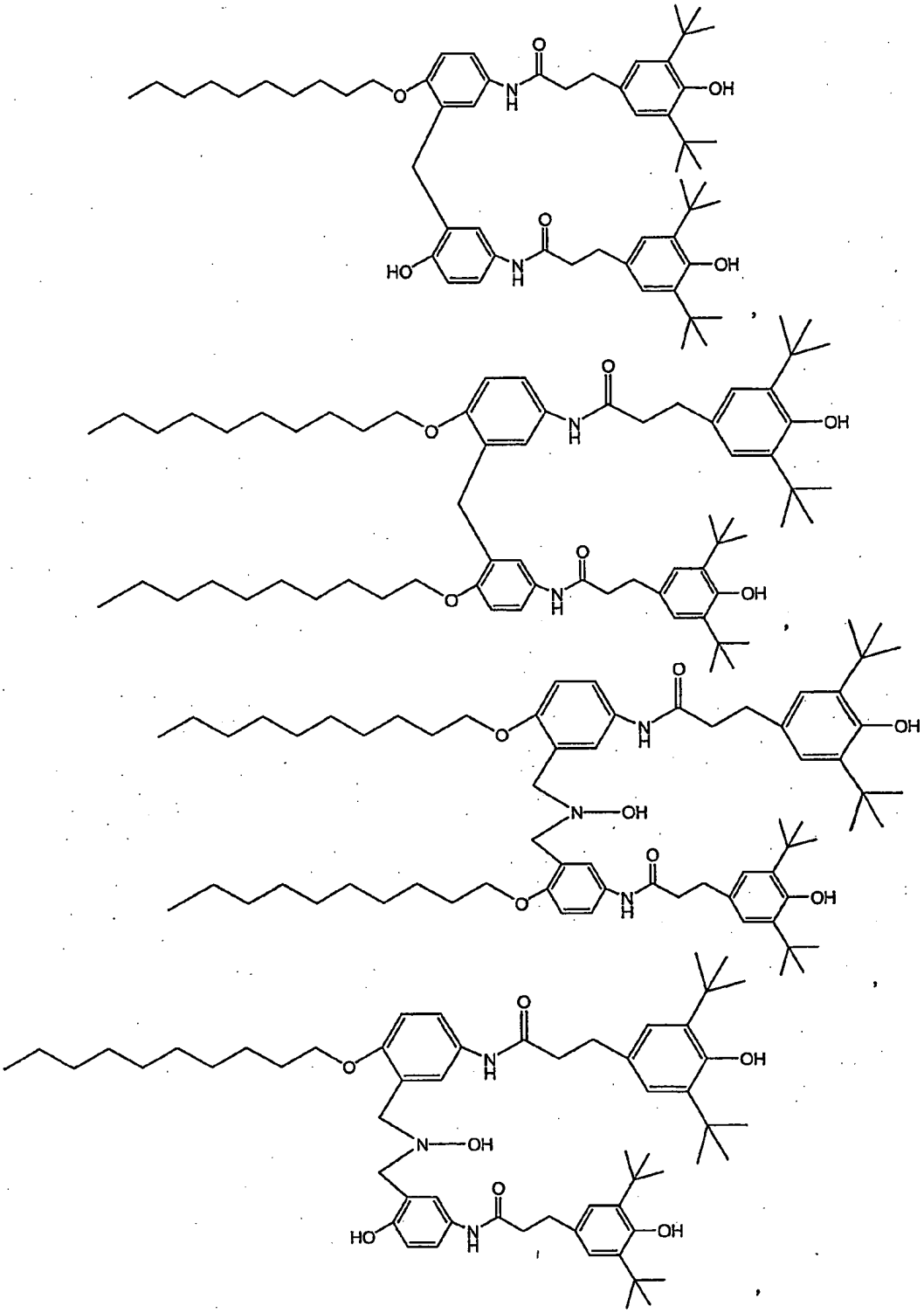
each R is independently an alkyl group;

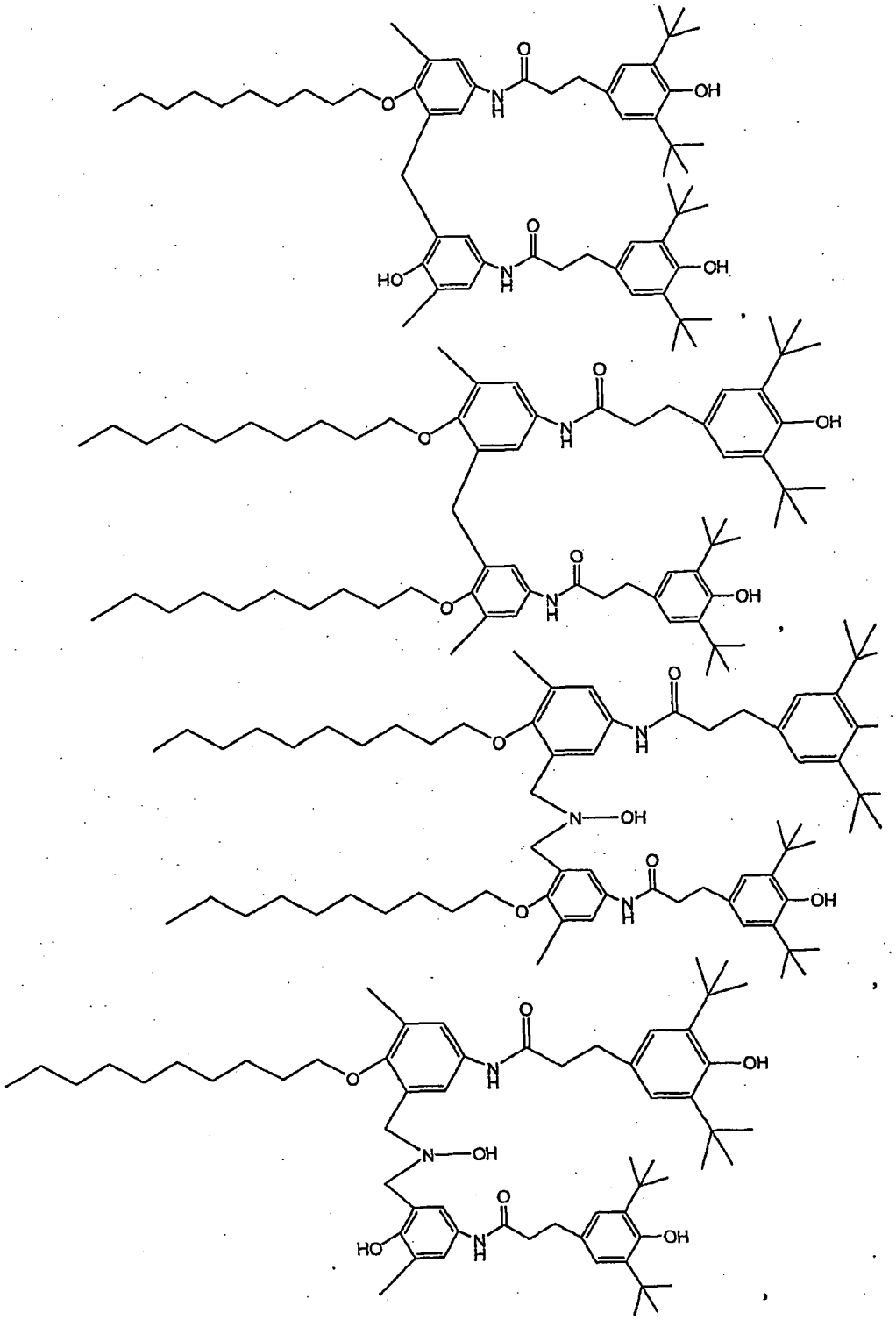
Y is -CR'V, -(CR" $_2$)p-phenylene-(CR" $_2$)$_p$-or -(CR" $_2$)$_p$N(OH)(CR" $_2$)$_P$;

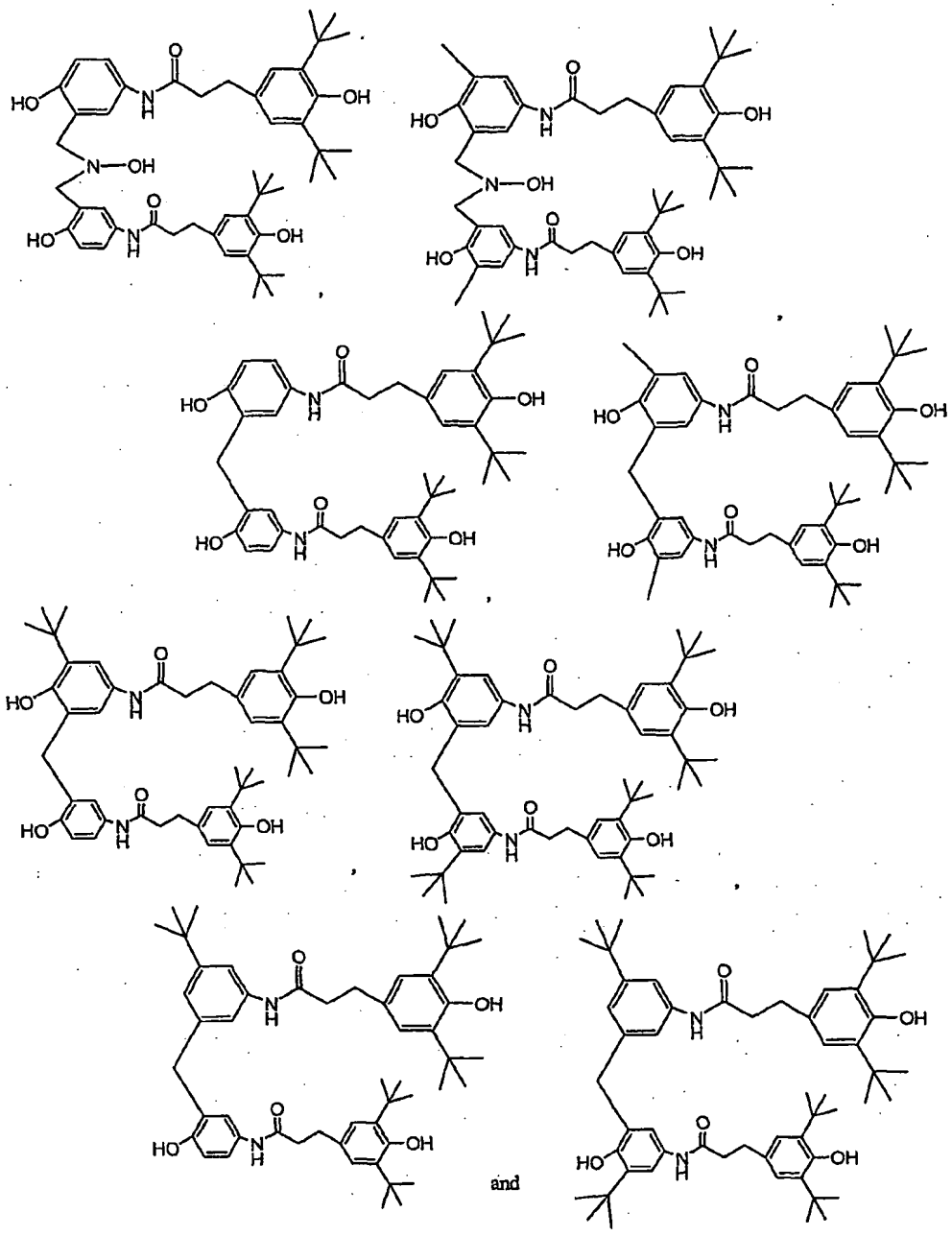
each R" is - H or alkyl; and

each p is independently an integer of 1 to 5.

11. The polymer of Claim 10, wherein the polymer is represented by a Structural Formula selected from:







and

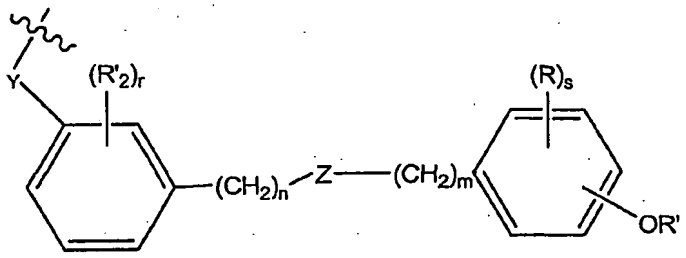
12. The polymer of Claim 7, wherein:

Z is -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -0- or -C(O)-;

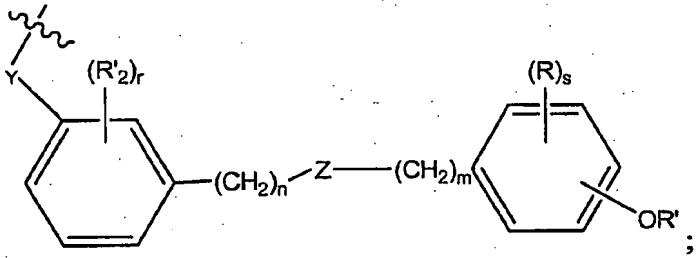
R' is -H;

each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl;

each R_2 is independently an optionally substituted alkyl or

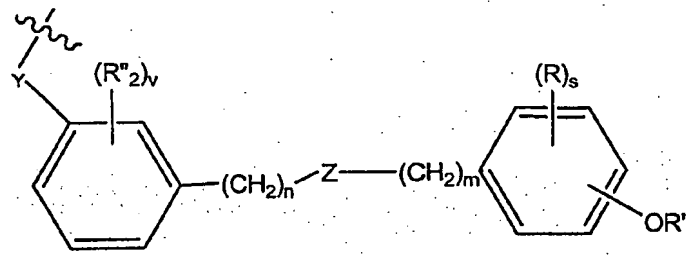


wherein at least one R_2 is

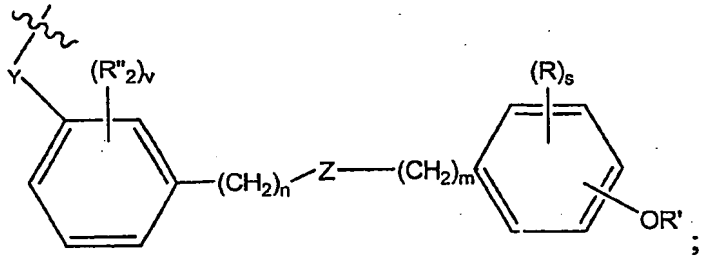


;

each R'_2 is independently -M'-X, an optionally substituted alkyl or

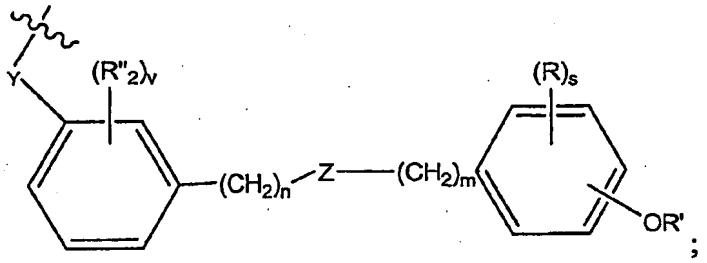


wherein at least one R'_2 is:



;

each $R"_2$ is independently -M'-X, an optionally substituted alkyl or



each M' is independently - H or alkyl;

X is -O-;

each Q is independently an optionally substituted Cl-ClO alkylene group;

each Q' is independently a bond or an optionally substituted ClO-ClO alkylene group;

each W is independently arylene, -O-, -S-, -NH-, -N(OH)-, -C(=N(OH))-, or abond;

each n and m are independently integers from 0 to 2;

each s and v are independently integers from 0 to 2; and

each r and q are independently integers from 1 to 3.

13. The polymer of Claim 12, wherein:

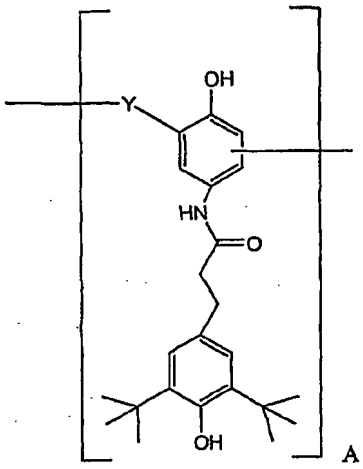
Z is -C(O)NH- or -NHC(O)-;

each R is independently an alkyl or an alkoxycarbonyl; and

s is 2.

14. The polymer of Claim 13, wherein each R is independently an alkyl group.

15. The polymer of Claim 14, wherein the polymer comprises a repeat unit represented by the following Structural Formula:



wherein:

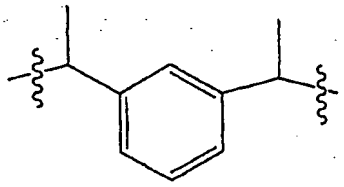
A is an integer of 3 or greater;

Y is -CR'Y, -(CR" $_2$)$_p$-phenylene-(CR" $_2$)$_p$-or -(CR" $_2$)$_p$N(OH)(CR" $_2$)$_p$;

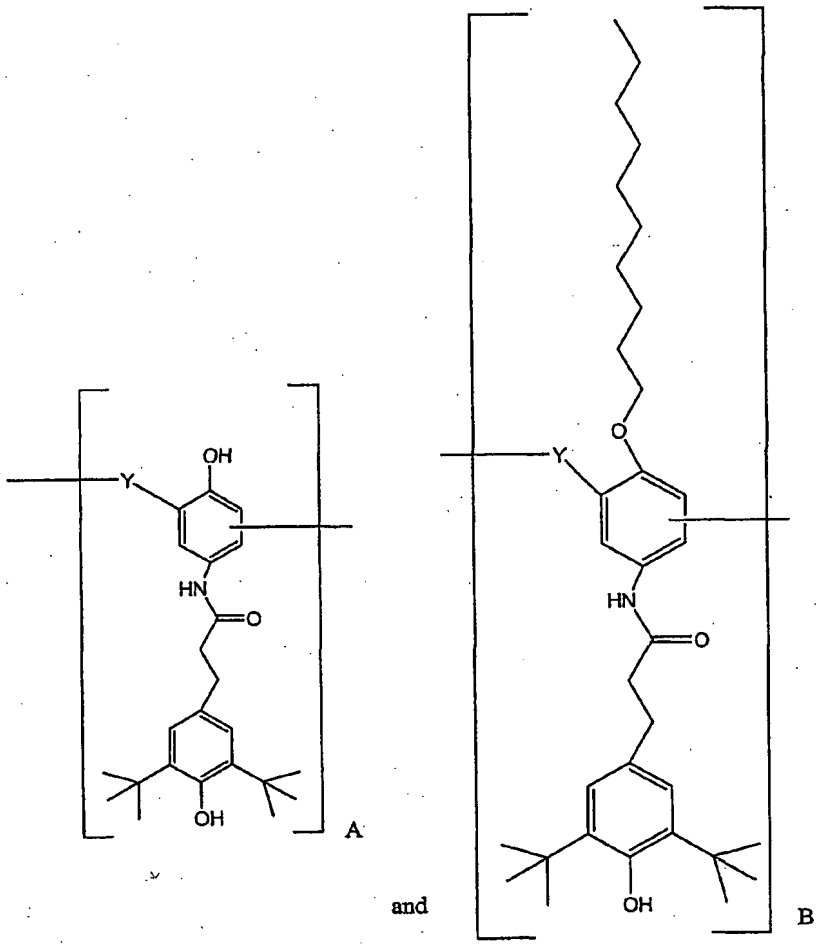
each R" is - H or alkyl; and

each p is independently an integer of 1 to 5.

16. The polymer of Claim 15, wherein Y is -CH_2, -$CH_2N(OH)CH_2$- or



17. The polymer of Claim 14, wherein the polymer comprises repeat units represented by the following Structural Formulas:



wherein:

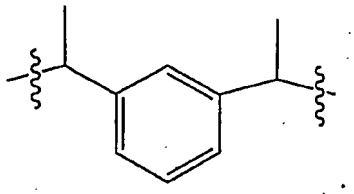
A and B are integers of 1 or greater and the sum of A and B is 3 or greater;

Y is -CR' V , -(CR' '$_2$)$_p$-phenylene-(CR''$_2$)$_P$-or -(CR" $_2$)$_P$N(OH)(CR" $_2$)$_P$;

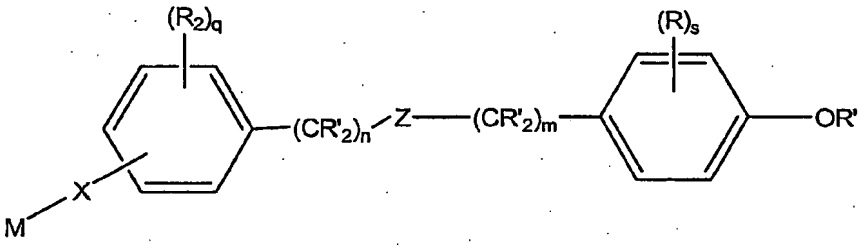
each R" is - H or alkyl; and

each p is independently an integer of 1 to 5.

18. The polymer of Claim 17, wherein Y is -CH $_2$, -CH$_2$N(OH)CH$_2$- or



19. A composition comprising compound one represented by the following Structural Formula:

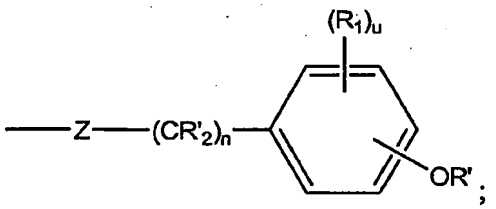


wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond;

each R' is independently -H or optionally substituted alkyl;

each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted

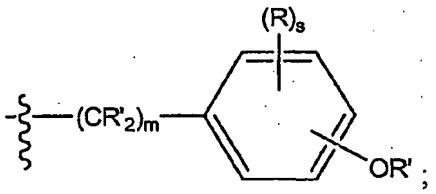


ester, -OH, -NH_2, -SH, or ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, -NH_2 or -SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, -NH_2 or -SH;

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -O-, -S-, -NR'- or -C(O)OC(O)-;

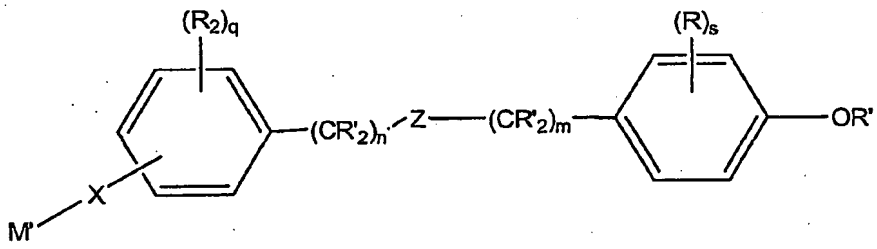
M is an alkyl or 

;

each n and m are independently integers from Oto 6;

each s, q and u are independently integers from Oto 4;

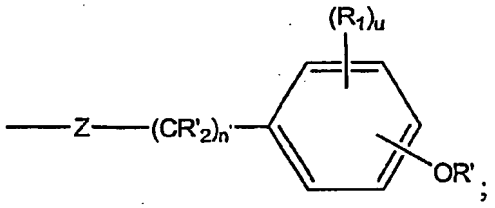
and compound two represented by the following Structural Formula:



wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -O-, -S-, -C(O)OC(O)- or a bond;

each R ' is independently -H or optionally substituted alkyl;

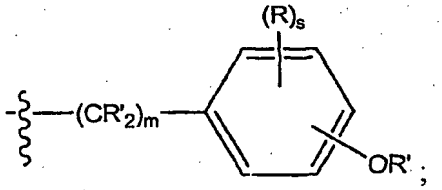
each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH, or 

;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

X is -C(O)O-, -OC(O)-, -C(O)NU'-, $-NR^5C(O)-$, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

M' is a -H, alkyl or 

;

each n and m are independently integers from Oto 6; and

each *s*, q and u are independently integers from Oto 4.

20. The composition of Claim 19, wherein:

each Z is independently -C(O)O-, -OC(O)-, -C(O)NH-, -NHC(O)-, -NH-, -O- or -C(O)-;

R' is -H;

each R is independently an optionally substituted alkyl or optionally substituted alkoxycarbonyl;

each R_2 is independently an optionally substituted alkyl;

X is -0-;

M is an alkyl;

M' is - H or alkyl;

each n and m are independently integers from Oto 2; and

each s and q are independently integers from Oto 2.

21. The composition of Claim 20, wherein:

each Z is independently -C(O)NH- or -NHC(O)-;

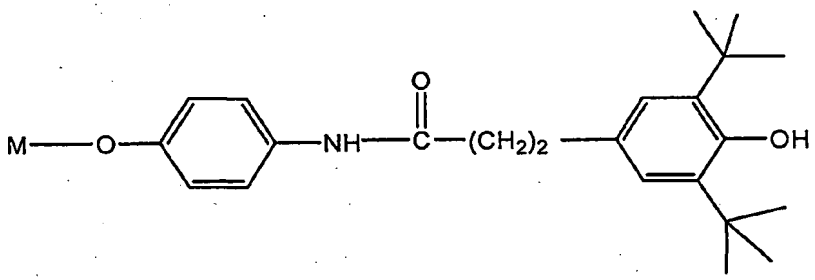
each R is independently an alkyl or an alkoxycarbonyl;

each R_2 is independently an alkyl; and

s is 2.

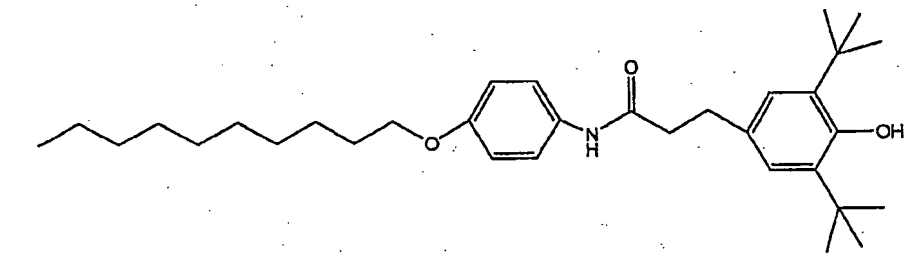
22. The composition of Claim 21, wherein each R is independently an alkyl group.

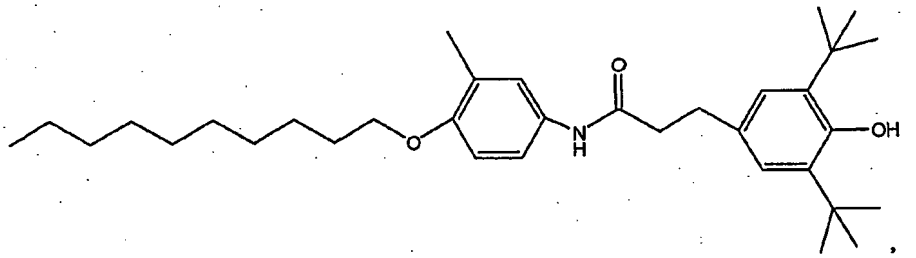
23. The composition of Claim 22, wherein compound one is represented by the following Structural Formula:

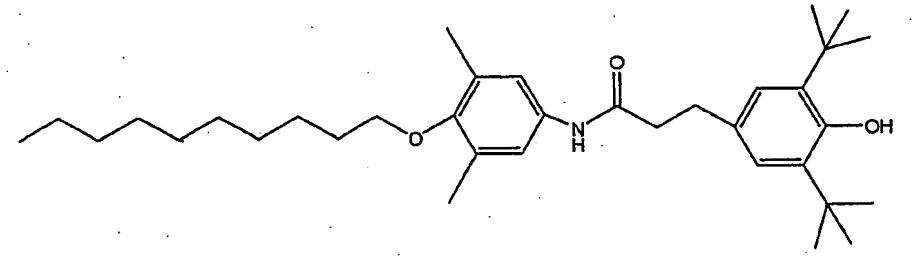


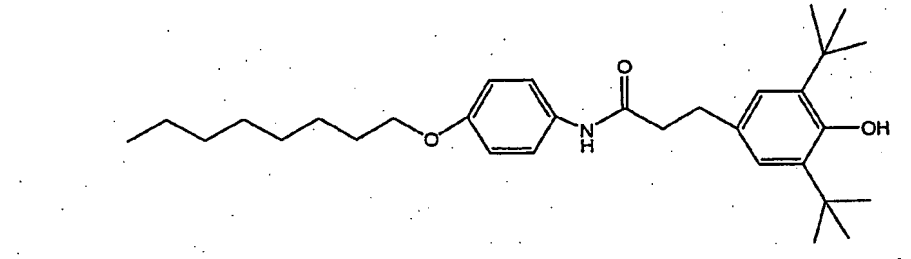
wherein M is a C1 to C20 linear or branched alkyl chain.

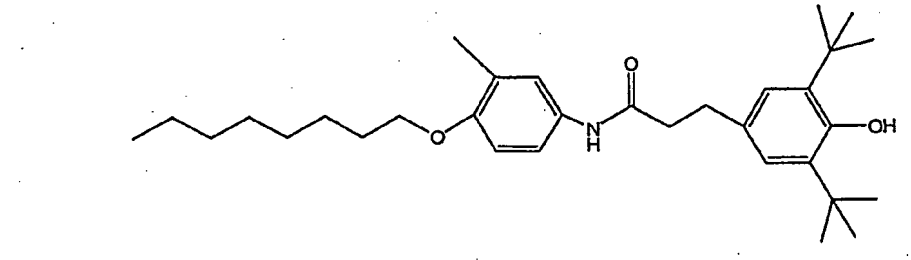
24. The compound of Claim 22, wherein compound one is represented by a Structural Formula selected from:

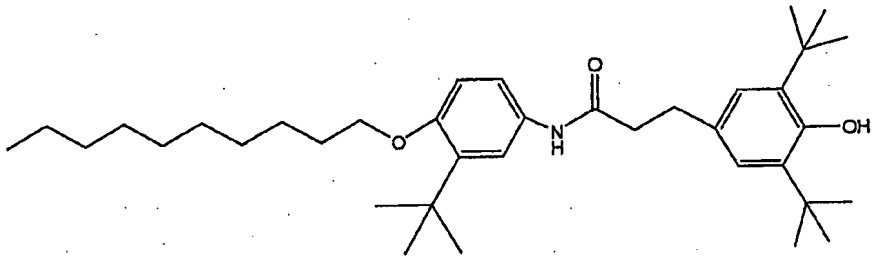


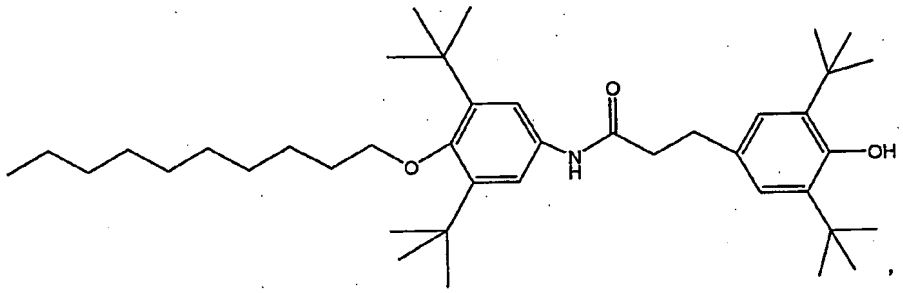


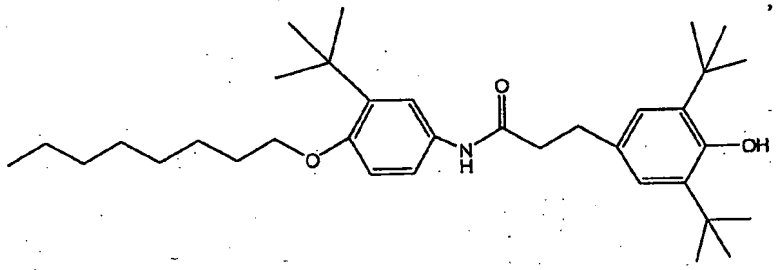


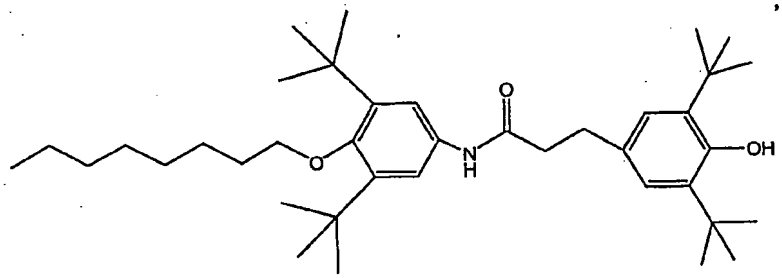


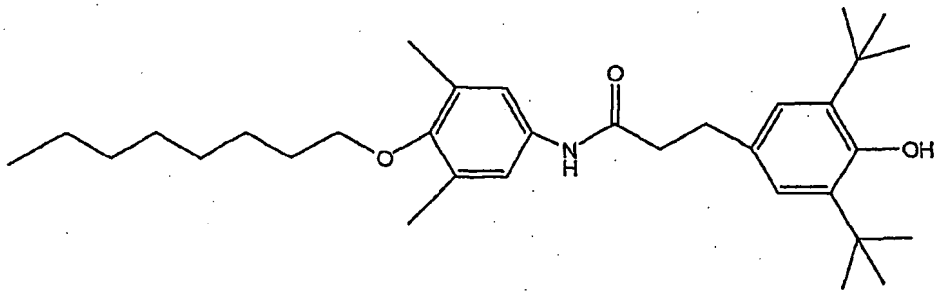




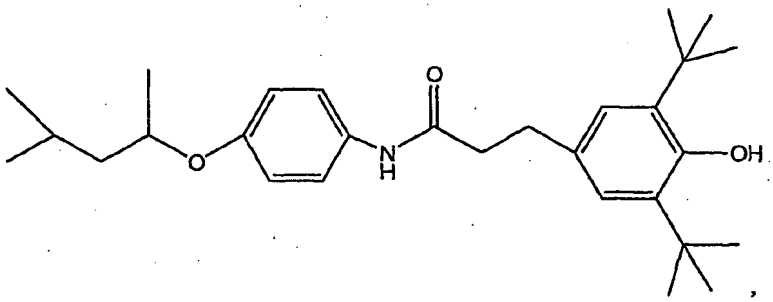




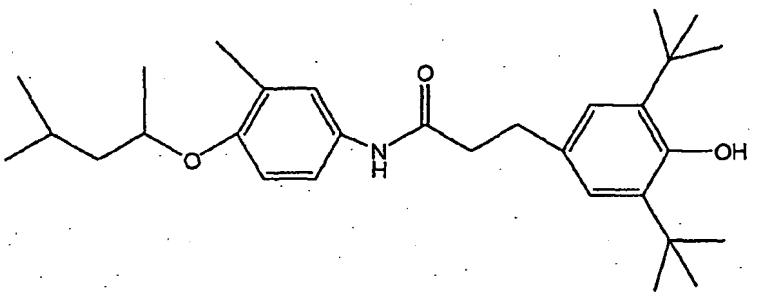




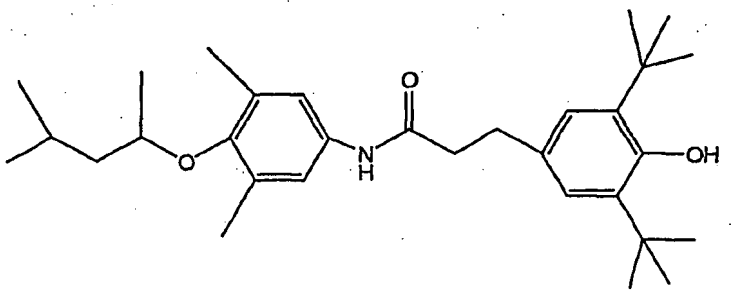
,



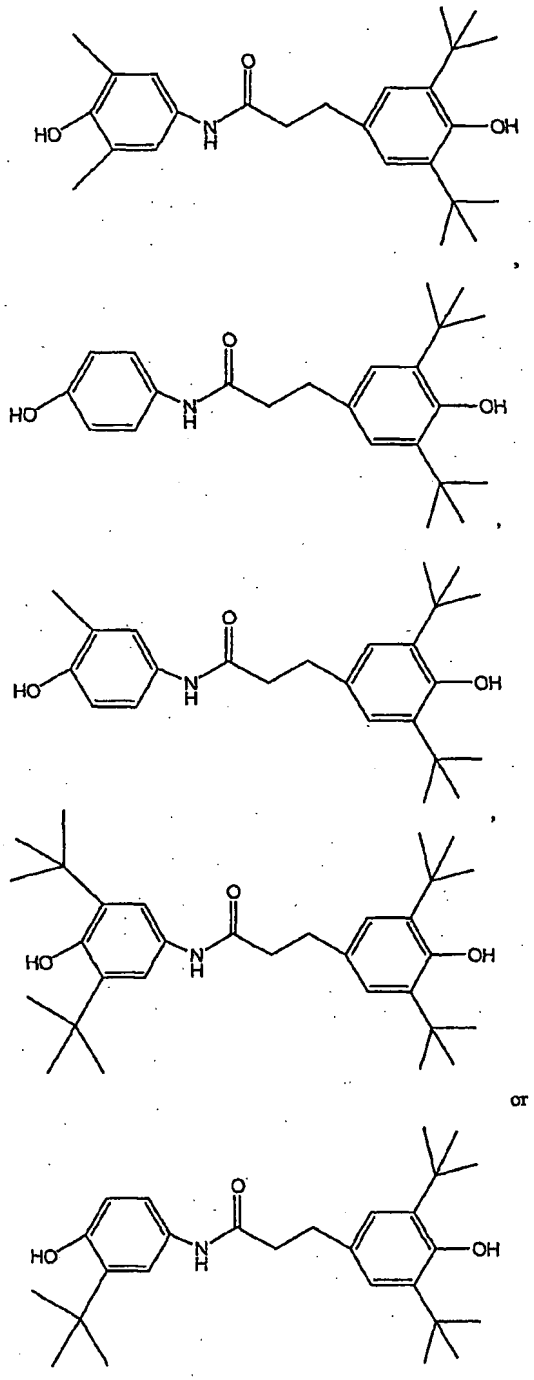
,



or



25. The compound of Claim 24, wherein compound two is represented by a Structural Formula selected from:

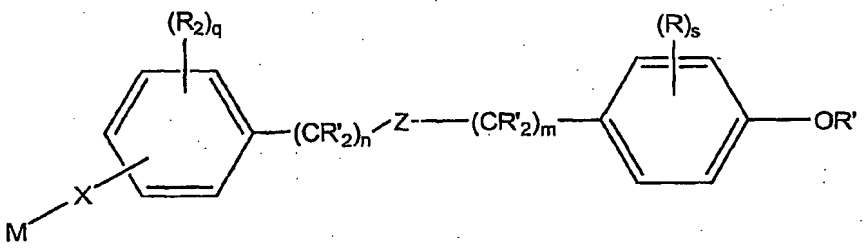


or

26. The compound of Claim 25, wherein the weightrweight ratio of compound onexompound two is 1:1, 1:2, 1:3, 1:5 or 1:10.

27. The compound of Claim 26, wherein the weight: weight ratio of compound onercompound two is 1:2.

28. A method of inhibiting oxidation in an oxidizable material comprising combining the oxidizable material with a compound represented by the following Structural Formula:

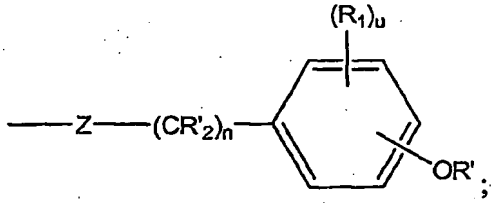


wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond;

each R' is independently -H or optionally substituted alkyl;

each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted

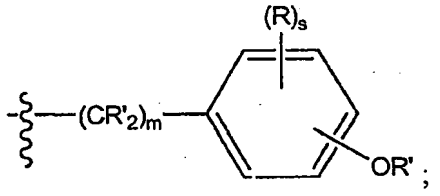


ester, -OH, $-NH_2$, -SH, or ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

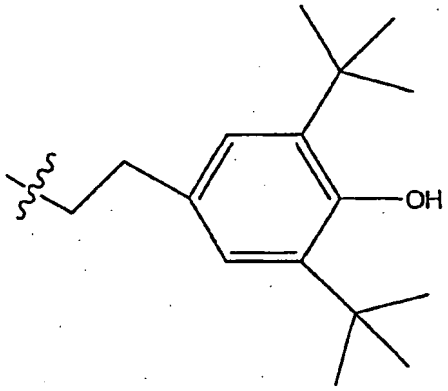
each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NRO(O)-, -NH'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

M is an alkyl or  ;

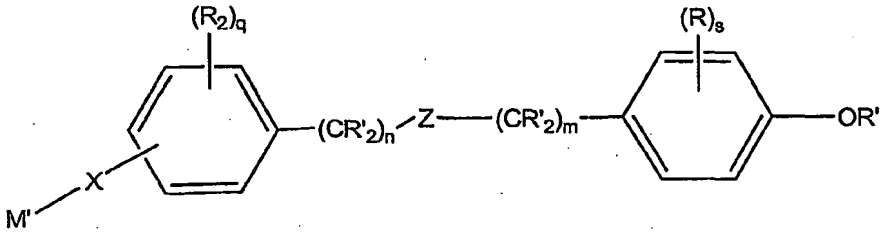
each n and m are independently integers from Oto 6; and

each s, q and u are independently integers from Oto 4;



wherein M is not when X is -C(O)O- or-OC(O>.

29. A method of inhibiting oxidation in an oxidizable material comprising combining the oxidizable material with a polymer represented by the following Structural Formula:

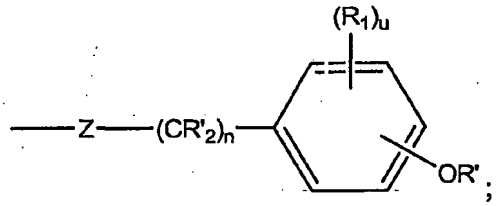


wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond;

each R' is independently -H or optionally substituted alkyl;

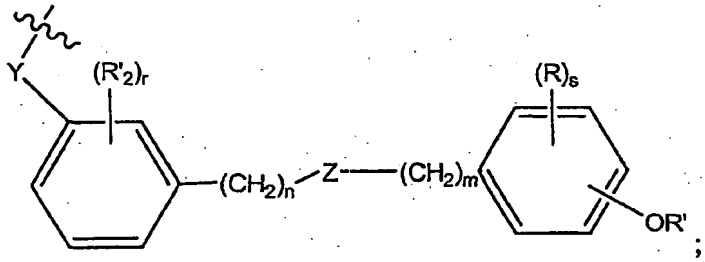
each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted



ester, -OH, $-NH_2$, -SH, or ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH or



;

each R'_2 is independently -M-X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH or -;

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

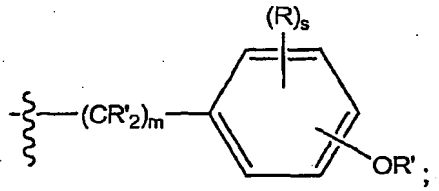
each Y is independently Q-W-Q';

each Q is independently an optionally substituted C1-C20 alkylene group;

each Q' is independently a bond or an optionally substituted C1-C20 alkylene group;

each W is independently arylene, -O-, -S-, -NR'-, -N(OR')-, -C(=N(0R'))-, -C(O)NR'-, -NR'C(O)-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -C(O)OC(O)-, or a bond;

each M' is independently -H, alkyl, or

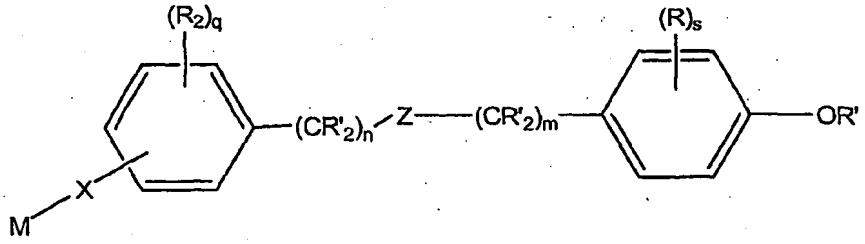


each n and m are independently integers from Oto 6;

each s, q and u are independently integers from Oto 4; and

r is an integer from Oto 4.

30. A method of inhibiting oxidation in an oxidizable material comprising combining the oxidizable material with a composition comprising compound one represented by the following Structural Formula:

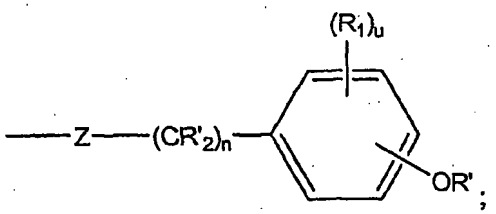


wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond;

each R' is independently -H or optionally substituted alkyl;

each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted

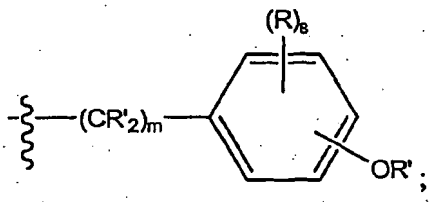


ester, -OH, $-NH_2$, -SH, or ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

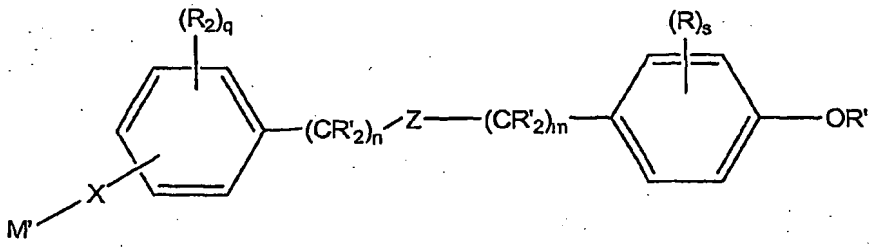
X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

M is an alkyl or  ;

each n and m are independently integers from Oto 6;

each s, q and u are independently integers from Oto 4;

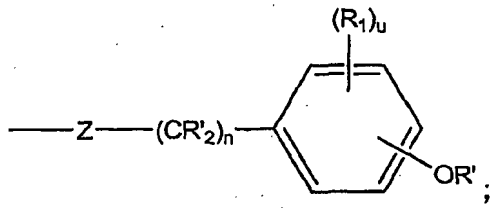
and compound two represented by the following Structural Formula:



wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond;

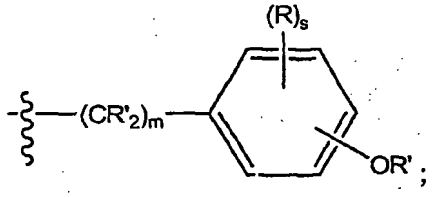
each R' is independently -H or optionally substituted alkyl;

each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH, or  ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, $-OH_5$ $-NH_2$ or -SH;

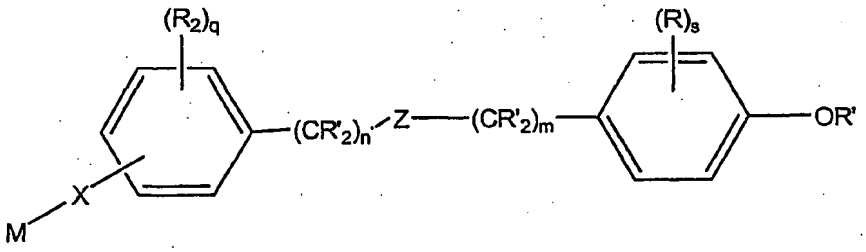
X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -O-, -S-, -NR'- or -C(O)OC(O)-;

M' is a –H, alkyl or  ;

each n and m are independently integers from Oto 6; and

each s, q and u are independently integers from Oto 4.

31. A method of making a compound represented by the following Structural Formula:

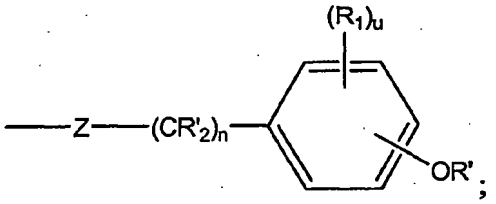


wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -O-, -S-, -C(O)OC(O)- or a bond;

each R' is independently -H or optionally substituted alkyl;

each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted

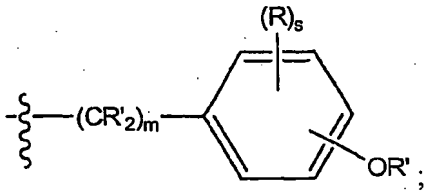


ester, -OH, $-NH_2$, -SH, or ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ or -SH;

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CH=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

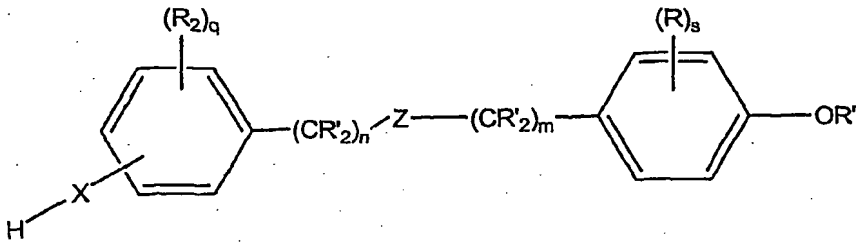
M is an alkyl or  ;

each n and m are independently integers from Oto 6; and

each s, q and u are independently integers from Oto 4;

comprising the steps of :

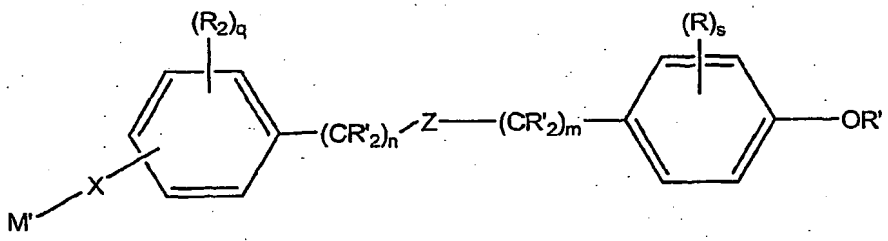
a) alkylating a compound represented by the following structural formula:



with a haloalkyl; and

b) isolating the alkylated compound.

32. A method of making a polymer represented by the following Structural Formula:

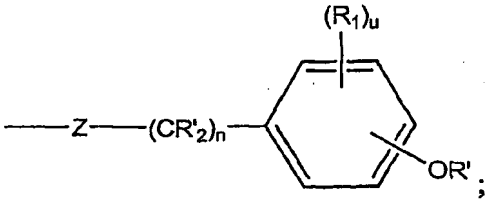


wherein:

Z is -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -0-, -S-, -C(O)OC(O)- or a bond;

each R ' is independently -H or optionally substituted alkyl;

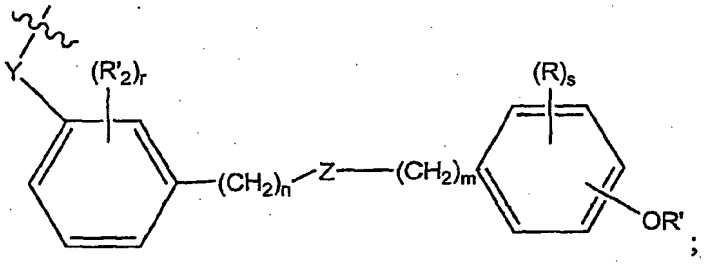
each R is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted



ester, -OH, $-NH_2$, -SH, or ;

each R_1 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$ Or-SH;

each R_2 is independently an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH or



;

each R'$_2$ is independently -M-X, an optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxycarbonyl, optionally substituted ester, -OH, $-NH_2$, -SH or -;

X is -C(O)O-, -OC(O)-, -C(O)NR'-, -NR'C(O)-, -NR'-, -CR'=N-, -C(O)-, -0-, -S-, -NR'- or -C(O)OC(O)-;

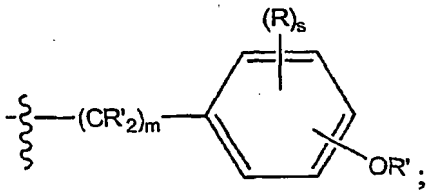
each Y is independently Q-W-Q';

each Q is independently an optionally substituted C1-C20 alkylene group;

each Q' is independently a bond or an optionally substituted C1-C20 alkylene group;

each W is independently arylene, -0-, -S-, -NR'-, -N(OR')-, -C(=N(0R'))-, -C(O)NR'-, -NR'C(O)-, -CR'=N-, -C(O)-, -C(O)O-, -OC(O)-, -C(O)OC(O)-, or a bond;

each M' is independently -H, alkyl, or



;

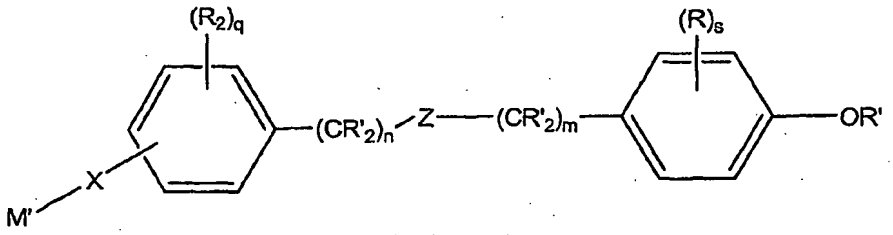
each n and m are independently integers from Oto 6;

each s, q and u are independently integers from 0 to 4; and

r is an integer from 0 to 4

comprising the steps of :

a) polymerizing a compound represented by the following structural formula:



in the presence of an aldehyde; and

b) isolating the polymer.

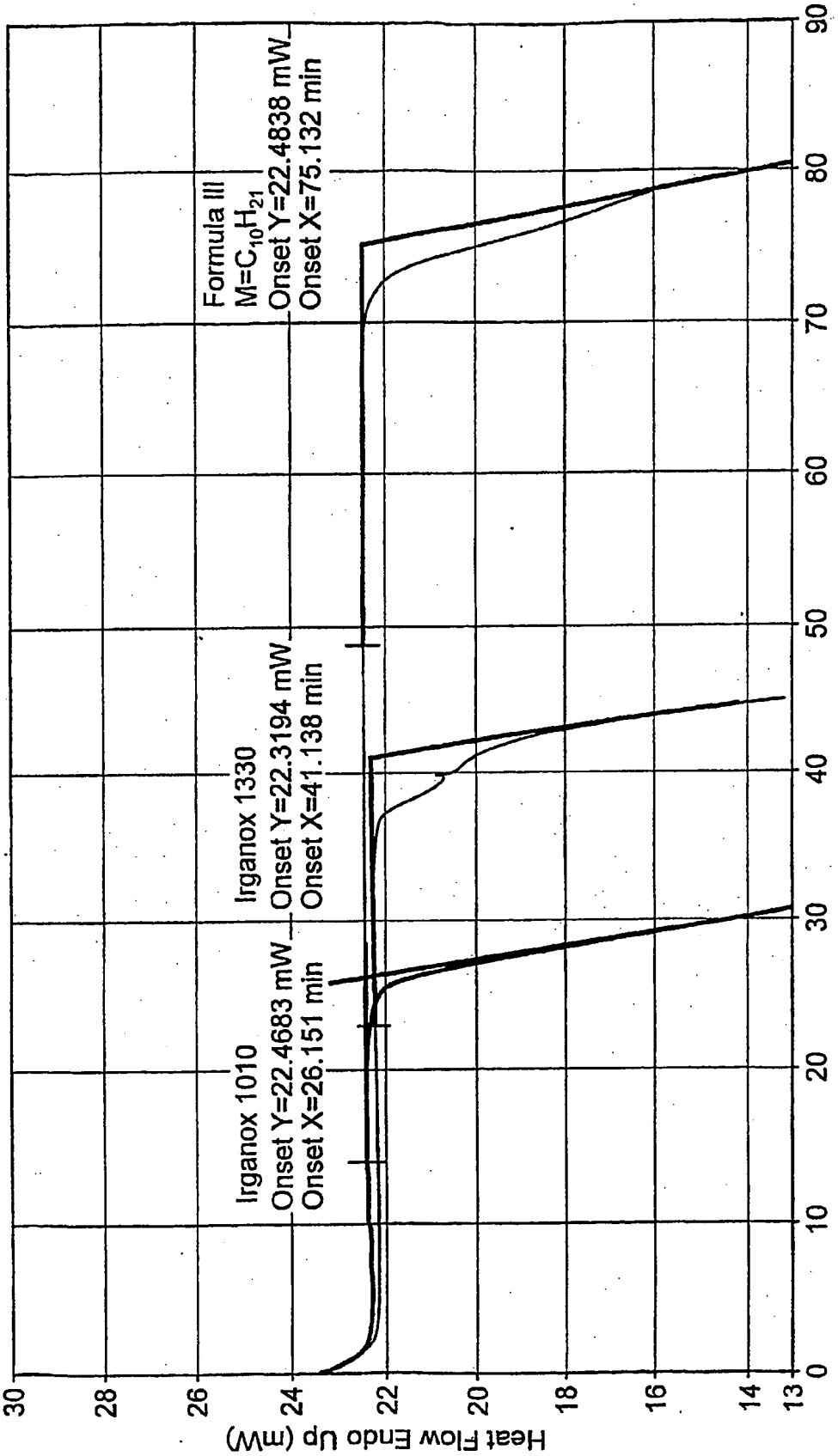

Formula III
M=C10H21
Onset Y=22.4838 mW
Onset X=75.132 min
Irganox 1330
Onset Y=22.3194 mW
Onset X=41.138 min
Irganox 1010
Onset Y=22.4683 mW
Onset X=26.151 min
Heat Flow Endo Up (mW)
Time (min)
30
28
26
24
22
20
18
16
14
13
0
10
20
30
40
50
60
70
80
90

FIG. 1

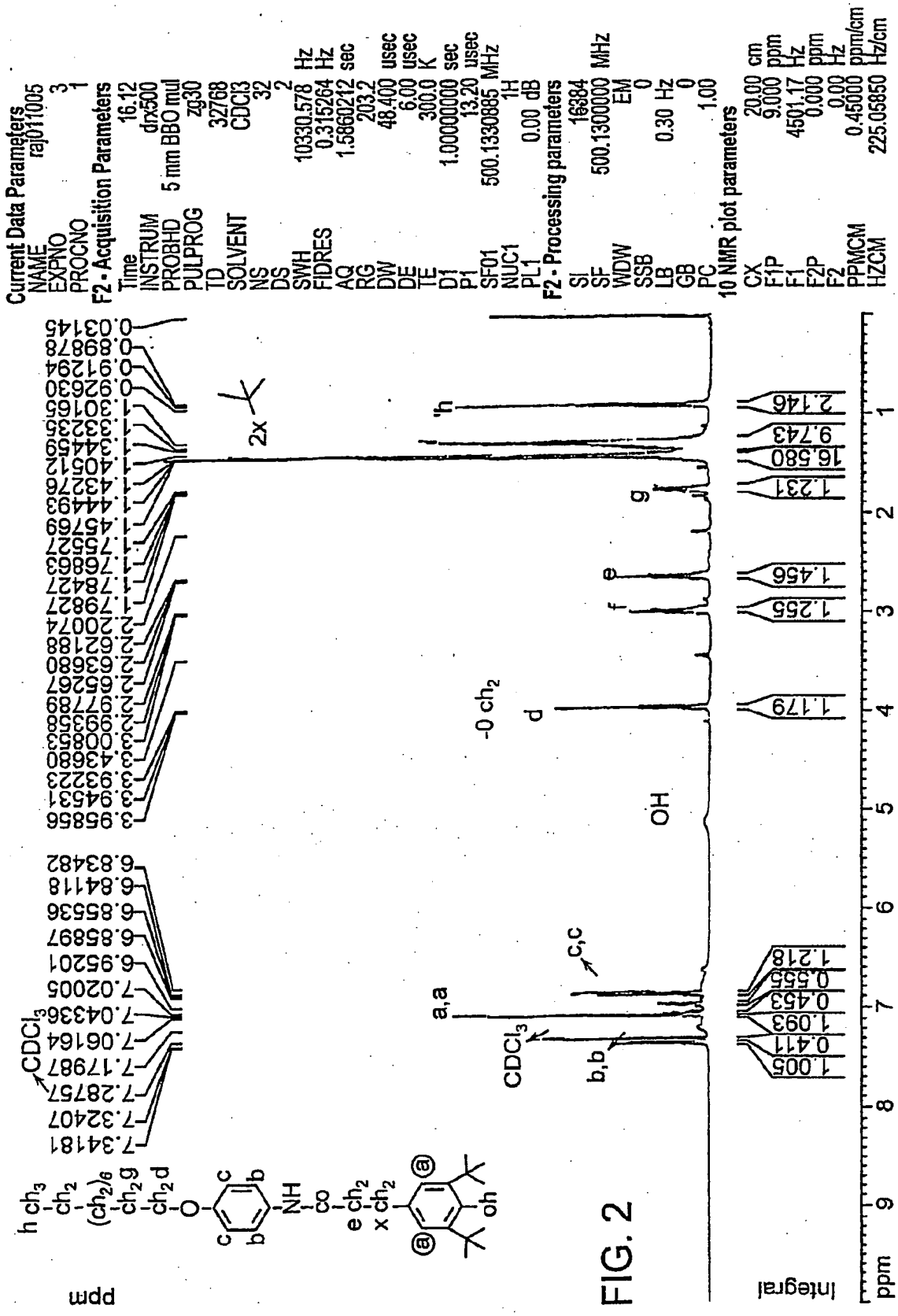

Current Data Parameters
NAME raj011005
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Time 16.12
INSTRUM drx500
PROBHD 5 mm BBO mul
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860212 sec
RG 203.2
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 13.20 usec
SFO1 500.1330885 MHz
NUC1 1H
PL1 0.00 dB
F2 - Processing parameters
SI 16384
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 NMR plot parameters
CX 20.00 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05850 Hz/cm
2x
h
g
f
e
d
-O ch2
OH
c,c
a,a
CDCl3
b,b
CDCl3
h ch3
ch2
(ch2)6
ch2g
ch2d
O
c
b
NH
co
e ch2
x ch2
oh
ppm
Integral

FIG. 2

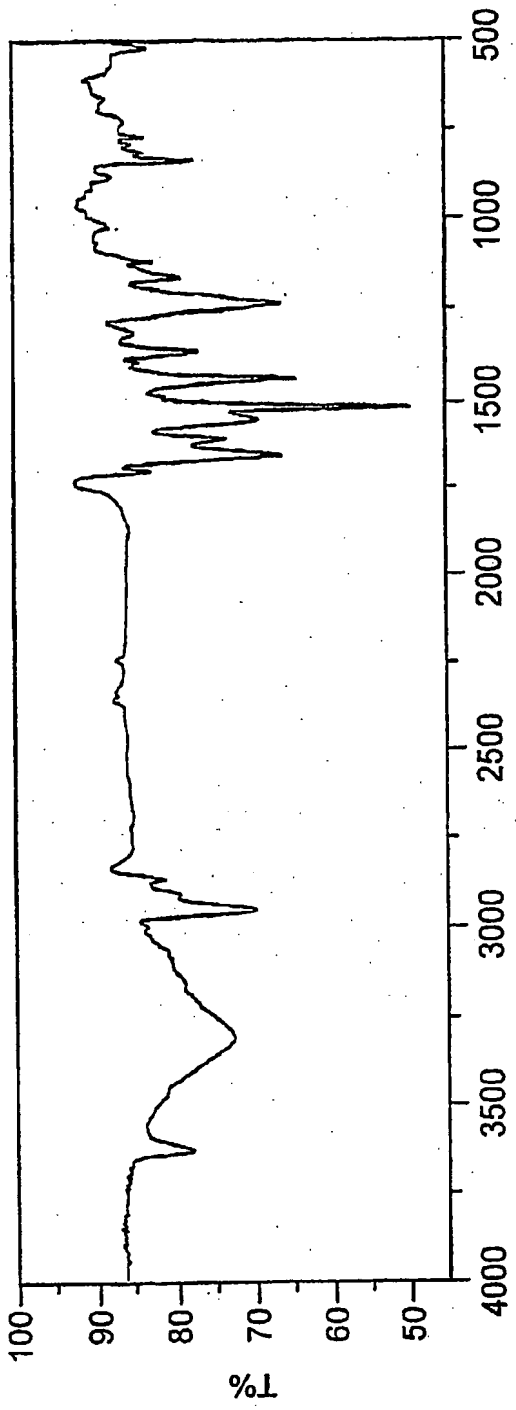


FIG. 3

PNX5E105

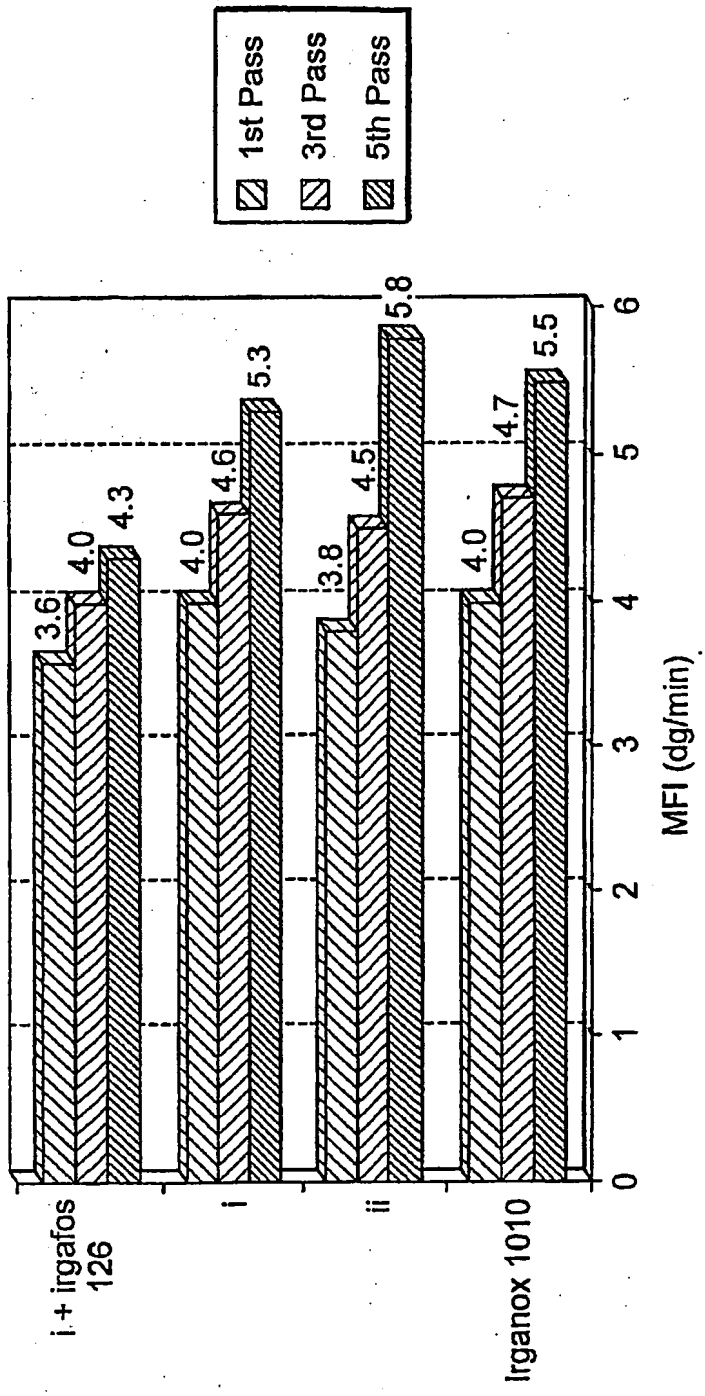

1st Pass
3rd Pass
5th Pass
3.6
4.0
4.3
4.0
4.6
5.3
3.8
4.5
5.8
4.0
4.7
5.5
0
1
2
3
4
5
6
MFI (dg/min)
i + irgafos 126
i
ii
Irganox 1010

FIG. 4

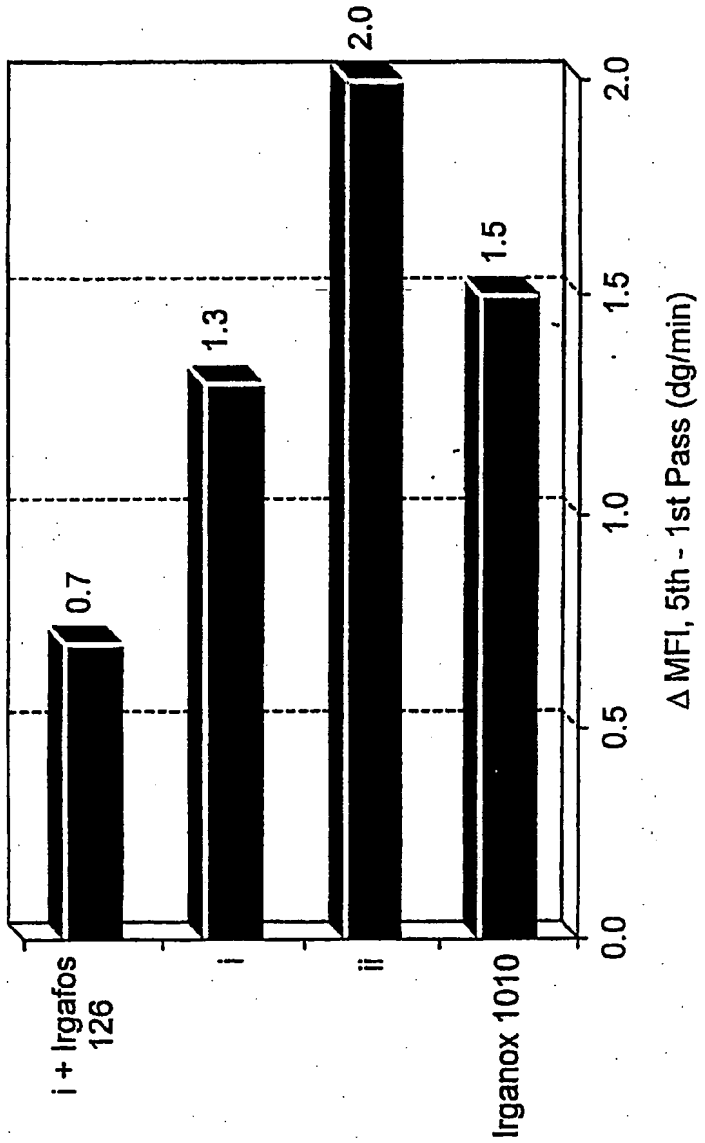

2.0
1.3
1.5
0.7
0.0
0.5
1.0
1.5
2.0
Δ MFI, 5th - 1st Pass (dg/min)
i + Irgafos 126
i
ii
Irganox 1010

FIG. 5

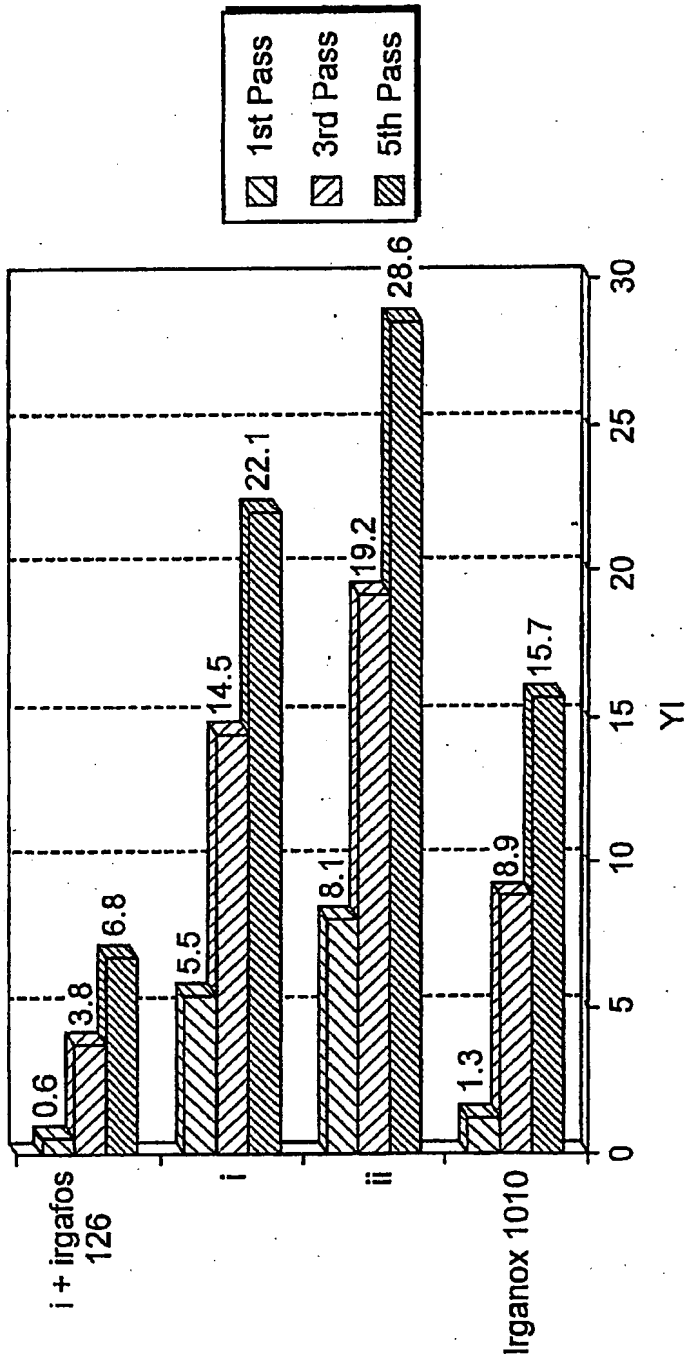

1st Pass
3rd Pass
5th Pass
0.6
3.8
6.8
5.5
14.5
22.1
8.1
19.2
28.6
1.3
8.9
15.7
0
5
10
15
20
25
30
YI
i + irgafos 126
i
ii
Irganox 1010

FIG. 6

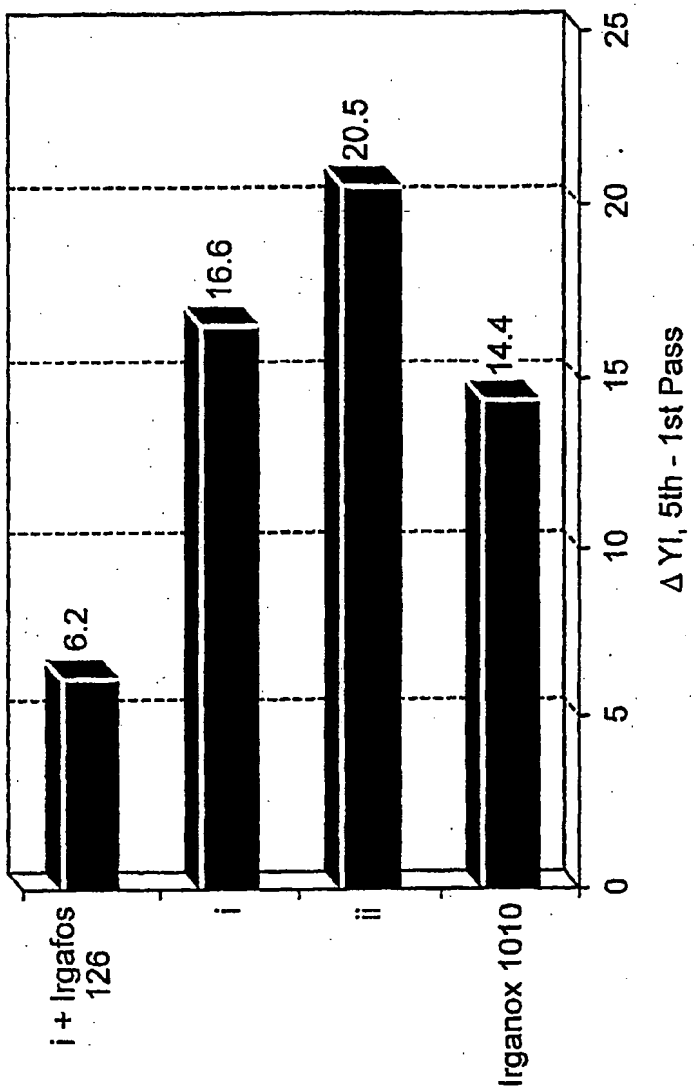

6.2
16.6
20.5
14.4
0
5
10
15
20
25
Δ YI, 5th - 1st Pass
i + Irgafos 126
i
ii
Irganox 1010

FIG. 7

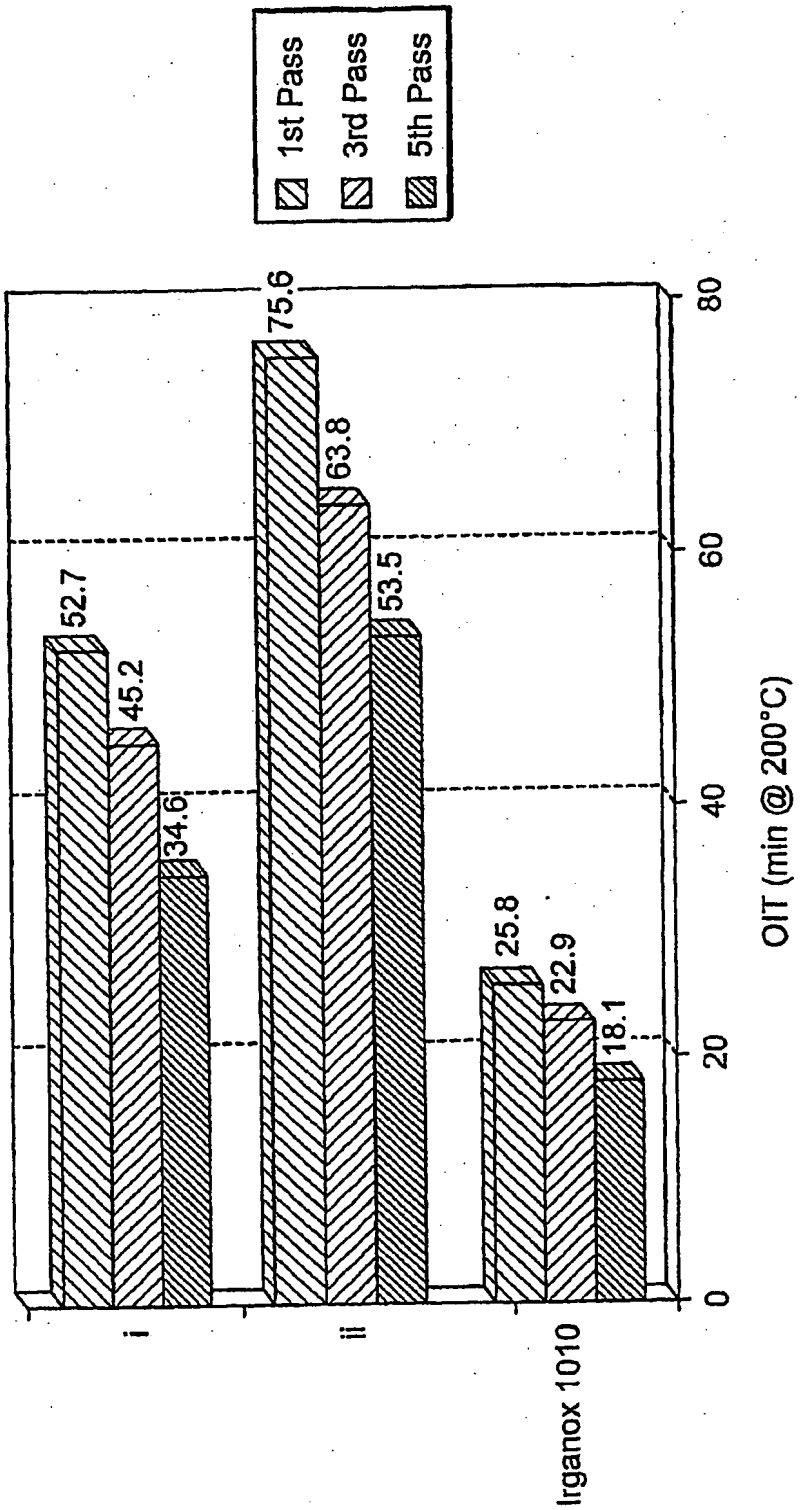

1st Pass
3rd Pass
5th Pass
52.7
45.2
34.6
75.6
63.8
53.5
25.8
22.9
18.1
0
20
40
60
80
OIT (min @ 200°C)
i
ii
Irganox 1010

FIG. 8

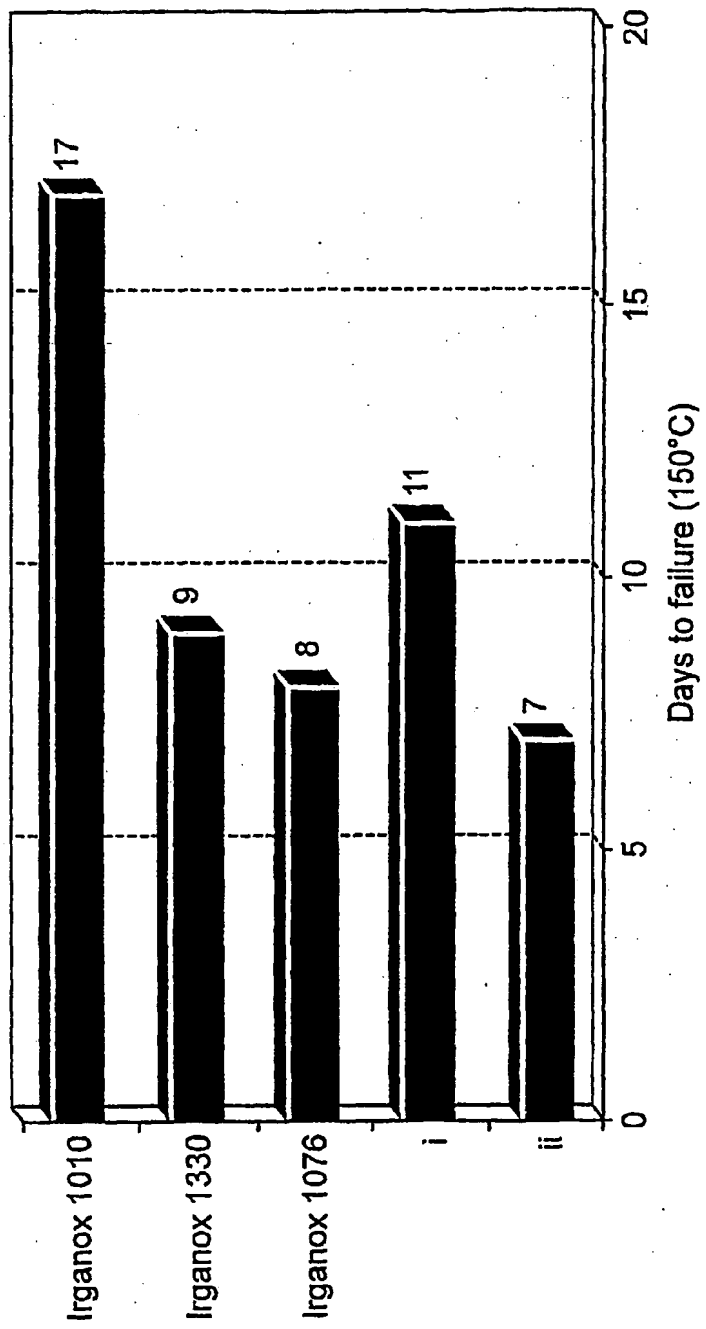

Days to failure (150°C)
0
5
10
15
20
17
9
8
11
7
Irganox 1010
Irganox 1330
Irganox 1076
i
ii

FIG. 9

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(71) Applicant *(for all designated States except US)*: **POLNOX CORPORATION** [US/US]; 333 Aiken Street, Lowell, Massachusetts 01854 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **KUMAR, Rajesh** [IN/US]; 820 Skyline Drive, Apartment 16, Dracut, Massachusetts 01826 (US). **CHOLLI, Ashok, L.** [US/US]; 6 Rosemary Lane, Chelmsford, Massachusetts 01824 (US).

(74) Agents: **PIERCE, N., Scott** et al.; HAMILTON, BROOK, SMITH & REYNOLDS, P.C., 530 Virginia Road, P.O. Box 9133, Concord, Massachusetts 01742-9133 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
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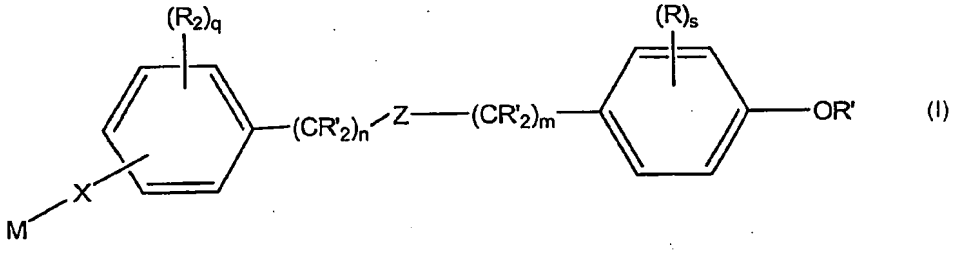
12 April 2007

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ALKYLATED AND POLYMERIC MACROMOLECULAR ANTIOXIDANTS AND METHODS OF MAKING AND USING THE SAME



(I)

(57) Abstract: Alkylated antioxidant macromolecules are represented by Structural Formula (I), wherein the variables are described herein. Also included are methods of making the molecules and methods of using the molecules as antioxidants.

WO 2006/104957 A3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2006/010985

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C235/38 C07C239/16 C08G8/08 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C C08G C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 459 704 A (PETERSON JANET BROOKS ET AL) 5 August 1969 (1969-08-05) page 1, left-hand column, line 31 - right-hand column, line 39; claims 1,6,11,12; example 19	1,28
X	US 5 834 544 A (LIN CHUNG-YUAN [US] ET AL) 10 November 1998 (1998-11-10) cited in the application examples 4,5	1,28
X	US 4 094 857 A (WOLFE JR JAMES RICHARD) 13 June 1978 (1978-06-13) column 4, lines 26,27,31,32; claims 1-5,8,9; example 3	1

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
22 November 2006	19/12/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax (+31–70) 340–3016	Ginoux, Claude

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/010985

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 770 785 B1 (DESAI SHROJAL MOHITKUMAR [IN] ET AL) 3 August 2004 (2004-08-03) cited in the application column 1, line 65 - column 2, line 23; examples 2-5,7 column 2, lines 58-67	1,28
X	V.V.PIROZHENKO ET AL.: "NMR Study of Topomerization of N-Aroyl-p-Benzoquinonemonoimines" RUSSIAN JOURNAL OF ORGANIC CHEMISTRY., vol. 31, no. 11, 1995, pages 1514-1519, XP002408364 USCONSULTANTS BUREAU. Compound Ie	1-4
X	G.M. COPPINGER ET AL: "Photo-Fries Rearrangement of Aromatic Esters" JOURNAL OF PHYSICAL CHEMISTRY, vol. 70, no. 11, November 1966 (1966-11), pages 3479-3489, XP002408365 USAMERICAN CHEMICAL SOCIETY Table V, 16th and 17th compounds page 3489, left-hand column, paragraph 1	1,2
X	R. SPANO ET AL.: "Substituted Anilides of 3-Monoethyl Ester of 4-Hydroxyisophthalic Acid" JOURNAL OF MEDICINAL CHEMISTRY., vol. 15, no. 5, 1972, pages 552-553, XP002408366 USAMERICAN CHEMICAL SOCIETY. WASHINGTON. compounds 15,16	1,2
A	EP 0 181 023 A1 (ENICHEM SINTESI [IT]; BOZETTO IND CHIM [IT]) 14 May 1986 (1986-05-14) examples 1,4	1-32
A	FR 2 183 973 A1 (SANDOZ SA [CH]) 21 December 1973 (1973-12-21) claims 1-6,9,11,12,18-22,25,27; examples 1,25,27	1-32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/010985

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		NL 7306151 A	13-11-1973
		US 3936479 A	03-02-1976